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Removal of Phosphates and Metals from Sewage Sludge

Research Report No. 28

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earch Program for the Abatement of Municipal Pollution under Provisions of the Canada-Ontario Agreement on Great Lakes Water Quality

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RESEARCH REPORTS

These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the Provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

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REMOVAL OF PHOSPHATES AND METALS FROM SEWAGE SLUDGE

by

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RESEARCH PROGRAM FOR THE ABATEMENT
OF MUNICIPAL POLLUTION WITHIN THE
PROVISIONS OF THE CANADA-ONTARIO
AGREEMENT ON GREAT LAKES WATER QUALITY

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ABSTRACT

Most of the metals and phosphorus in either unconditioned or conditioned final anaerobically digested sludges can be readily extracted by acid. The acid extract can be neutralized under controlled conditions of pH to yield a solid product low in organic material containing mostly iron and aluminum phosphates. By proper control of pH, it is possible to produce two solid products, one containing most of the iron and aluminum, and one containing most of the heavy metals.

Iron and phosphate can be separated and recovered from the crude inorganic product by known solvent extraction technology, or by alkali treatment. Costs are such that if metals and phosphates are removed from a sludge, then it is profitable to recover and recycle the iron and phosphate from the crude inorganic product. However, the value of recovered metals and phosphates is not sufficient to bear the cost of the entire process.

RÉSUMÉ

On peut facilement extraire par un acide la plus grande partie des métaux et du phosphore présents dans les boues finales, digérées en anaérobiose, qu'elles aient été conditionnées ou non. L'extrait acide peut être neutralisé, dans les conditions voulues de pH, pour donner un mélange solide, à faible teneur en matières organiques, et contenant surtout des phosphates de fer et d'aluminium. Par réglage convenable du pH, on peut obtenir deux produits solides, le premier contenant la plus grande partie du fer et de l'aluminium, l'autre, la plus grande partie des métaux lourds.

On peut séparer et récupérer le fer et les phosphates du produit minéral brut, en faisant appel aux techniques connues d'extraction par solvant, ou par traitement à la soude. Les coûts font que, si les métaux et les phosphates sont retirés d'une boue, il est alors profitable de récupérer et de recycler le fer et les phosphates du produit minéral brut. Toutefois, la valeur des métaux et des phosphates récupérés n'est pas de nature à neutraliser le coût d'exploitation de tout le procédé.

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CONCLUSIONS AND RECOMMENDATIONS

A process has been developed whereby metals and phosphates can be extracted with acid from anaerobically digested sludges, and the extract treated to precipitate a solid product which is low in organic material, and which consists mainly of ferric or ferrous phosphates. If the sludge has been alum-treated, the major component will be aluminum phosphates. Depending on the conditions of precipitation, heavy metals may be left largely in the filtrates, may be a part of the precipitated iron phosphate or may be precipitated separately.

Iron and phosphate can be recovered separately by the use of strong alkali solutions, or by using conventional known solvent extraction techniques. The conditions and techniques likely to be most useful are described.

Cost of removing most of the metals and phosphate from anaerobic sludges are estimated to be $30-$35 per million gallons of influent (activated or mixed sludges were not tested in this study). Separation and recovery of iron and phosphate from the metal-phosphate solid product is estimated to yield a net income of about $10 per million gallons of influent. Therefore, if removal of metals and phosphates from sludges is practiced, it is profitable to recover and recycle the iron (or aluminum) and phosphate from the crude inorganic product rather than disposing of it.

Cost-benefit studies on the removal of metals and phosphates from sludges before disposal or incineration should be carried out. If any significant benefit is apparent, studies similar to the one described in this report should be made using the sludge produced by the largest plants, since it is likely that it is only for large treatment plants that further sludge processing of this kind might be warranted. The metal and phosphate removal process described here should then be piloted - the facilities existing at the Canada Centre for Inland Waters, Wastewater Technology Centre, would probably be quite satisfactory.

1. INTRODUCTION

With the advent of chemical treatment for the removal of phosphates in wastewater treatment plants, the sludges produced from these plants will now contain the bulk of the phosphate in the original influent streams. In addition to its phosphate content, the sludge will also contain most of the metallic cations entering in the influent stream, as well as the metallic cations such as iron or aluminum which may have been added as treating chemicals to effect phosphate removal, or as coagulants. Whether the sludges are mixed sludges, activated sludges, or primarily anaerobic digested sludges, they will all contain the bulk of the metals and phosphorus that originally entered the treatment plant.

The role of metals, particularly the heavy toxic metals such as copper, chromium and zinc in the sludges is not yet completely appreciated. In the concentrations usually found in treatment plant liquids, there is not usually any adverse affect on biological activity in the treatment plant processes themselves. However, the metals become concentrated to a considerable degree in the sludge and some of them frequently reach appreciable levels (e.g. 5% by weight of dry solids or more). The case of anaerobically digested sludge is particularly interesting because of the reduction in sludge volume during digestion, and the correspondingly increased metal content. It is, therefore, questionable whether sludges from anaerobic digestion can be used repeatedly for agricultural purposes on a given piece of land. There is also some evidence that leachates and run-off waters from sludge land disposal sites may contain undesirably high quantities of dissolved heavy metals and of phosphates. Certainly, the thickener underflow from an anaerobic digester prior to dewatering or disposal contains amounts of copper and chromium which, if they became soluble, would appear to far exceed the recommended maximum limits for successful continued bacterial action. See Barth et al (1), Poon and Bhayani (10), or Sudo and Aiba (17).

Two problems can be identified with respect to the metals and phosphate content of sludges and the ultimate disposal of the sludge. If it were possible to remove most of the heavy metal content from the sludge this might be desirable, particularly in cases where the sludges are to be

used for agricultural purposes or where there is more than a normal contamination with heavy metal impurities. In addition, there is the possibility that if iron or aluminum has been added for phosphate removal, these metals could be recovered and recycled within the treatment plant. The high phosphate content of sludges is sometimes also undesirable, for some of this material can leach out from sludge disposal sites, particularly if the sludge is fairly alkaline or fairly acid, and ground waters may feed the phosphate pollution back into the watershed system. If the sludge is incinerated, then the ash from the incinerator will be rich in phosphate and heavy metals, and may well be a source of these materials, particularly for recycling the iron or aluminum for further use in phosphate removal.

There is not yet, to our knowldege, any process which offers workable technology for removing metals and phosphates from underflow sludges, or filter cake sludges. It would be a matter of some interest to develop technology for carrying out the removal of these materials from sludges, and then given the technology, evaluating whether or not this process would be likely to yield benefits commensurate with its costs.

2. OBJECTIVES

The principle objectives of this work fell into two categories. The first part of the study involved leaching of sludges from processes using iron or alum for phosphate precipitations. The second part of the study involved an examination of the extract from the leaching of the sludge in order to determine methods of extracting phosphate, iron or aluminum, and other metals from it. In this examination of the extract, particular attention was to be paid to the possible role of solvent extraction as a means of making separations between metallic cations, or of extracting phosphate from the aqueous extract.

Assuming that some successful technique of carrying out useful separations was developed, it was planned to investigate the economic implications of the results and to make some estimate of the potential value of recovered materials and the costs of the possible alternative processes based on leaching of final sludges.

3. NATURE OF THE PROBLEM

There are many kinds of sludge produced from waste treatment plants, and a wide variation in sludge compositions depending on the waste source and the type of process. However, from the viewpoint of their metals content these sludges can be characterized roughly according to whether iron or aluminum have been used for phosphate precipitation, and whether or not the sludge has been produced with an anaerobic digestion step. This latter distinction is of some importance because the sludge volume is considerably less when anaerobic digestion is used, with correspondingly higher contents of metals and phosphates. In addition, anaerobic sludges may have some metals, e.g., iron, in lower valence states, with a corresponding difference in behaviour from oxidized sludges.

Because of the higher metal concentrations an anaerobic sludge was selected for this study. Inasmuch as iron is likely to be a major chemical used for phosphate removal, a plant employing ferric iron addition for this purpose was also desired. Both of these requirements were met by the North Toronto Treatment Plant of the Municipality of Metropolitan Toronto, Department of Works, Water Pollution Control Division. This plant has employed phosphate removal using ferric chloride addition for nearly three years. It produces a sludge which is the product of primary and secondary treatment combined with anaerobic digestion, which is disposed of on a land site. The sludge underflow from the final digesters is conditioned by the addition of ferric chloride and lime prior to vacuum filtration. Therefore sludge was available both as an underflow without conditioning chemicals added, and as filter cake which contained conditioning chemicals. All work reported in this study was done using material from this plant.

Recent literature does not reveal any reports of investigations undertaken for the same objectives as those set out for this study. Presumably, the removal of metals and phosphate from treatment plant sludges represents a stage of treatment which is not yet being seriously considered. Most tertiary treatment is devoted to further purification of effluents. Less attention has been paid to reducing problems of sludge disposal by removing from the sludge some of the possibly undesirable chemical constituents. Because so little attention seems to have been

given to this problem it was necessary to investigate nearly every aspect of behaviour in exploring techniques of extraction and recovery of chemicals from sludges. Also as a consequence of this lack of previous work, a great many alternatives were possible, and therefore a number of choices had to be made on the basis of qualitative knowledge or expectations. No doubt there are other ways of approaching the problem which are not considered in this report and which were not investigated. However, one approach has been worked out and is outlined in the following sections.

4. CHOICE OF RECOVERY METHODS FOR CHEMICALS

A typical anaerobic sludge in which iron has been used for phosphate removal contains about 7% iron, about 6% calcium and 11 - 12% of phosphorus (expressed as orthophosphate*) based on dry sludge weight. After conditioning for filtration, the sludge on a dry weight basis can contain 8 - 9% or more of iron, about 11 - 12% calcium and about 12% orthophosphate. In addition to these major elements, the sludge also contains small but significant amounts of aluminum, zinc and copper, and minor amounts of many other metals.

In order to separate some of these components, and particularly the phosphate, from the bulk of the solids, one can solubilize orthophosphate either into strongly alkaline or strongly acidic solutions. In the former case, the orthophosphate and much of the aluminum and zinc would go into solution, but very little of any other metals. However, it might also be expected that a very substantial proportion of the organic matter might become soluble or colloidal in form in strongly alkaline solutions. On the other hand, in an acid solution not only the orthophosphate would go into solution, but essentially all the metallic cations. However, only the lower molecular weight organic compounds might be expected to go into solution and might represent a relatively small percentage of the organic matter. For this reason, acid extraction was selected as the first step in treating a sludge.

Having obtained from a sludge an acid extract in which most of the metallic cations are present together with many soluble organic materials, two possibilities are now evident. Either this extract can be treated in order to remove desired components, for example, particular metallic cations or particular anions by chemical means such as precipitation as insoluble salts, or the extract can be subjected to nonchemical steps such as solvent extraction, distillation, etc. If solvent extraction is used, then the organic impurities in the extract are likely to cause problems and contamination in the extraction system. However, the possibility also exists that chemical methods can be used to further

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*Throughout this report, phosphorus is assumed to be present in the sludge as the appropriate form of orthophosphate. It is acknowledged that this assumption is not always entirely valid.

purify the solution, particularly by removing the bulk of the organic materials in the extract. Solvent extraction might then be applied to the product of this further chemical purification step. Given the very low economic value of the principle components, that is iron and phosphate, it is apparent that in any recovery process the minimum consumption of reagents and the minimum number of processing steps are necessary if the costs of removal of these materials from sludges are not to be excessive.

It can be seen that there is a large number of alternate choices in techniques that might be used, in the order in which these recovery steps may be undertaken and in the choice of reagents to be used for various purposes. In addition, if iron is recovered and recycled, it must not also involve the recycling of the major part of any of the harmful constituents, for example, copper, or a resultant build-up in copper content in the treatment plant streams could result. Several alternatives are investigated in the work reported here, but by no means all of them. However, a sufficient range of conditions has been covered and a sufficient number of variables investigated to allow a better understanding of methods which might be successful in removing metals or phosphates from sludges. These results will also give some indication of where the major cost factors exist.

5. ACID EXTRACTION OF ANAEROBIC SLUDGES

5.1 Extraction of Conditioned Filter Cake

The filter cake sample used in all tests was taken on April 27th, 1973, across the length of the doctor knife of the rotary vacuum filter at the North Toronto Sewage Treatment Plant. This cake was estimated to be a product of the average influent flows during the month of March, 1973. During this period the plant handled about 11.8 mgd of raw sewage. Phosphorus removal was accomplished by addition of 7.2 mg/l of Fe as $FeCl_3$. In addition, about 2.6 mg/l of Fe as $FeCl_3$ was added prior to de-watering in the filter feed tank together with about 24 mg/l of 90% lime. Plant records indicate that the filter cake contained 17.2% dry solids, and when in steady operation the plant produced about 45 tons of dry sludge solids per week.

5.2 Sludge Characteristics

The dewatered sludge was analyzed according to standard methods. In order to establish reliable initial values for metals and phosphorus content, sludge digestion and subsequent analysis was carried out by three methods,

A. Nitric acid - sulphuric acid digestion

B. Nitric acid - perchloric acid digestion

C. Hydrochloric acid digestion

The only meaningful total carbon and COD values are obtained from the HCl digestion, since the oxidizing acids destroy organic material. Calcium values cannot be obtained when sulphuric acid is used for digestion because of calcium sulphate precipitation.

The results of analyses are given in Table 1. As expected, iron, calcium, aluminum, and phosphorus are the major inorganic constituents. Other metals total only about 4% of the solids, with zinc and copper being present in the largest amount. Metal analyses were all carried out by atomic absorption, while phosphorus analysis was done by the heteropoly blue method.

5.3 Acid Treatment of sludge

Preliminary tests to determine the degree of extraction of various constituents by treatment with hydrochloric or sulphuric acids

TABLE 1. ANALYSES OF DEWATERED SLUDGE
MOISTURE = 79.15%

Component		Concentration, mg/gm dry sludge		
		A	B	C
Total Iron	(Fe)	85.5	88.0	87.5
Phosphorus	(P)	39	40	38.5
Calcium	(Ca)	-	116	120
Aluminum	(Al)	-	-	11.8
Zinc	(Zn)	1.94	2.06	1.88
Copper	(Cu)	0.91	1.02	0.98
Chromium	(Cr)	0.39	0.40	0.41
Manganese	(Mn)	0.30	0.34	0.34
Nickel	(Ni)	-	Trace	-
Lead	(Pb)	-	Trace	-
Total Carbon in Extract		30.1	23.8	55.0
C O D		9.73	3.98	67.3
Residue after Digestion		318.6	111.6	229.9

were carried out using a standard sample amount equivalent to 20 gms of dry sludge solids in 1000 ml of reaction mixture. The mixture with added acid was agitated in an open reaction flask held in a constant temperature bath. Amounts of added acid were calculated on the basis of the stoichiometric requirement of calcium, ferric and zinc ions in the sludge, which for the standard 20 gram sample required 0.215 equivalents. (The aluminum equivalent was not included since at the time of these tests, Al analyses were not available. However, other cations, both inorganic and organic, are also present in unknown amounts and have not been included. Therefore, amounts of "excess" acid given are somewhat large, e.g., what is reported as 100% excess is probably actually about 75% excess, and 15% excess is approximately the stoichiometric equivalent on the basis of the major metallic cations. In this report, the term "excess acid" is a relative one used because it gives some indication of the acid consumption. Other possible acid usage parameters, such as titratable acid, for example, were not found to be satisfactory because of the strongly buffering nature of the solutions.)

With an 80% moisture content, it is apparent that one disadvantage in extracting the wet sludge would be the resulting dilute solutions obtained. One possible way to avoid this result is to pre-dry the sludge. Therefore, sludge was dried at 100°C, the dried sludge ground to 16 mesh, and 20 gram samples of this material were also tested.

The amount and rate of extraction of total iron and of phosphorus were used as indicators of the extraction efficiency. Results are shown in Figures 1 and 2 for four extraction tests, all at 25.5°C. Dried and "as-is" sludges were used in two tests, both with 100% excess HCl, which showed very clearly the detrimental effect of a pre-drying step on the ease of extraction of both iron and phosphates. Even after 3 hours only 70% extraction had been achieved from the pre-dried solids, whereas the undried sludge gave a 95% yield at the same conditions in 3 minutes. Other tests at other conditions confirmed the loss of easy solubility resulting from sludge drying. Tests were also carried out using 100% excess sulphuric acid and a 15% excess amount of hydrochloric acid. Results in Figures 1 and 2 show that hydrochloric and sulphuric acid perform equally well in dissolving iron and phosphates, but that some excess over the approximate stoichiometric equivalent is required.

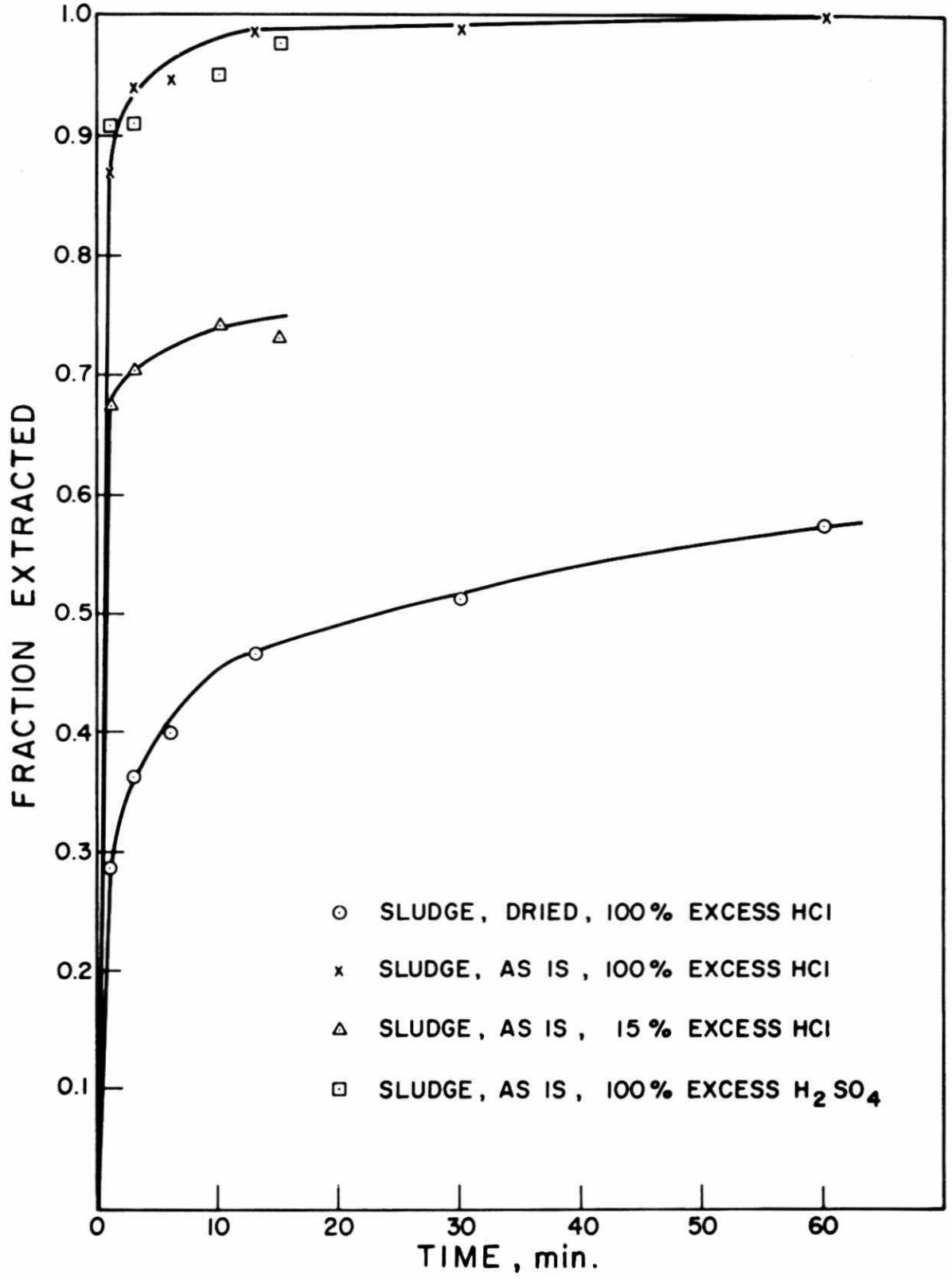

FIGURE 1. PRELIMINARY TESTS OF IRON EXTRACTION RATES FROM CONDITIONED FILTER CAKE
(Leach Conditions - Sample weight equivalent to 20 gm dry solids in 1000 ml slurry, 25.5°C)

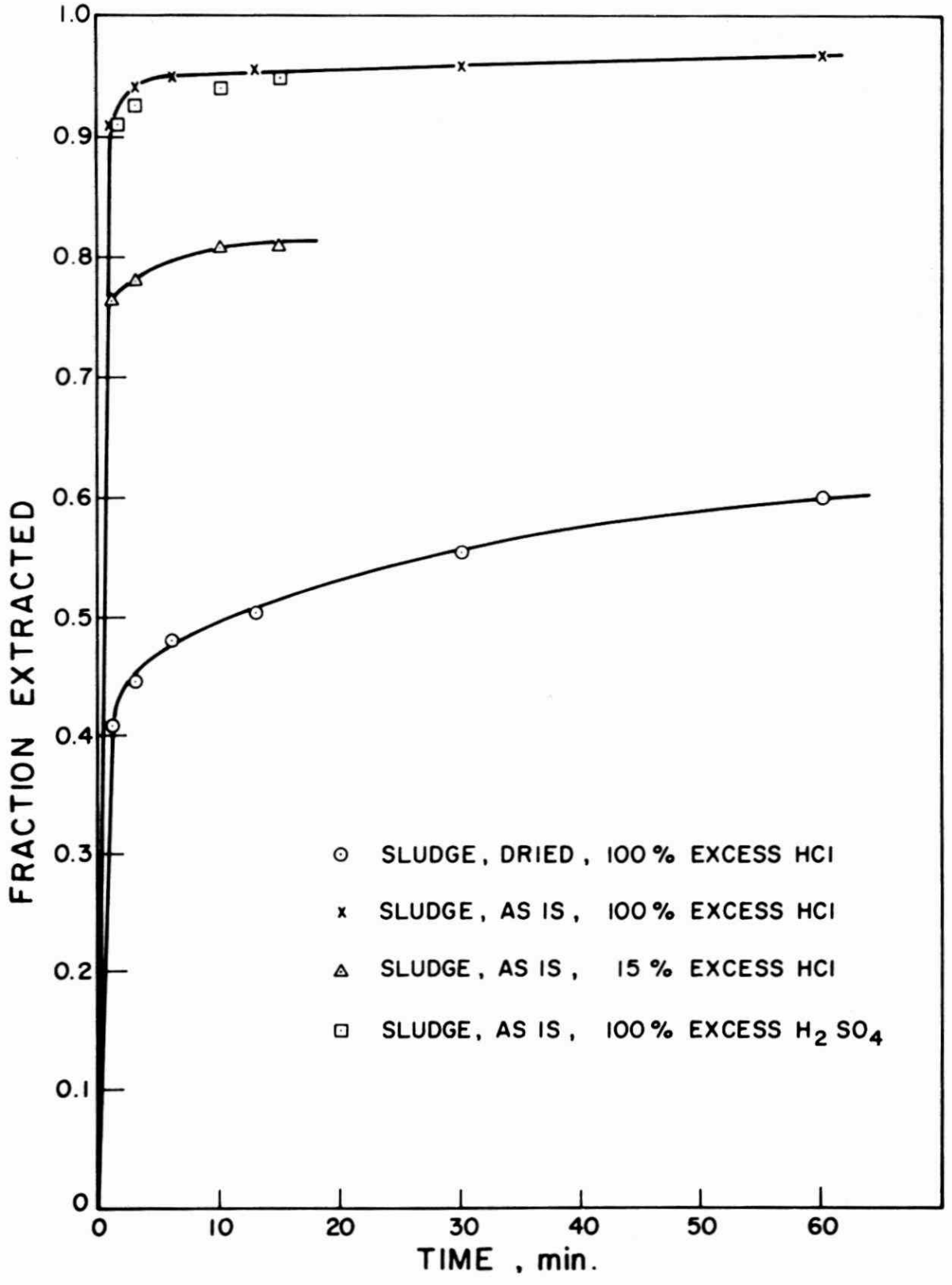

FIGURE 2. PRELIMINARY TESTS OF PHOSPHATE EXTRACTION RATES FROM CONDITIONED FILTER CAKE (Leaching conditions - Sample weight equivalent to 20 gm dry solids in 1000 ml slurry, 25.5°C)

On the basis of these preliminary tests, only sulphuric acid was used in further work. The use of sulphuric acid is clearly advantageous because of its low cost, because of its ability to remove much of the calcium as $CaSO_4$ precipitate, and because of the improved filterability of the leach mixture when sulphuric acid was used (due probably to the large amount of granular $CaSO_4$ formed).

Additional tests and observations indicated that sludges leached for long times at high acid excess showed very poor filterability. Reduction of leach time and reduction of acid strength both improved filterability. However, about 50% excess acid was required to obtain high extractions of iron or phosphorus in short times. Hot acid extraction of sludge did not improve filterability, but if the sludge was extracted at room temperature, then heated to boiling and filtered hot, a dramatic improvement in filterability resulted.

5.4 Determination of Optimal Leach Conditions

Optimal leach conditions were established using criteria of completeness of extraction of iron and phosphorus and filterability. Extraction was carried out at room temperature using a standard leaching time of 15 minutes and the procedure already described, then the reaction mixture was heated to boiling (requiring about a further 15 minutes), and filtered hot. Amount of excess acid addition was the independent variable.

Filterability was measured according to the methods described in Manual No. 20, "Sludge Dewatering" of the Water Pollution Control Federation (1969), Page 30. In our tests, a 7 cm diameter Gooch funnel was used together with #40 Whatman filter paper. A constant filtration pressure differential of 31.5 cm Hg was maintained, and time vs filtrate volume readings were taken for a 100 ml sample of "homogeneous" slurry. The formula applying is

$$(r_\mu) = \frac{2\,b\,P\,A^2}{c}$$

Where b = slope of a plot of θ/V vs V where θ is filtration time and V is filtrate volume

P = filtration pressure, gm/cm^2 ($428\ gm/cm^2$)

A = filtration area, cm^2 ($38.5\ cm^2$)

c = weight of dry sludge/unit volume of solution, gm/cm^3

μ = filtrate viscosity, poises

r = specific cake resistance, sec^2/gm

For comparative purposes of these tests, a sludge filterability index was defined as the ratio of the ($r\mu$) product in any test to the ($r\mu$) product obtained for the original sludge when untreated or unheated.* Hence, since the ($r\mu$) product is a filtration resistance coefficient, the sludge filterability index is a direct measure of the change in resistance to filtration compared to the original untreated sludge.

Sludge Filterability Index (SFI)

$$= \frac{(r\mu) \text{ measured}}{(r\mu) \text{ original sludge}}$$

Results of tests at the standardized leach conditions are shown in Figure 3. The region of 50% to 60% excess acid represents optimal conditions, in that the filterability index is a minimum (about 0.33) and the maximum extraction of iron and phosphorus possible at these conditions has been nearly attained.

A sludge leached at room temperature under the above standard conditions with 55% excess acid and with c = 0.02 gm/cm^3, had an SFI value before heating of 3.7, and after bringing to boiling an SFI value of 0.3 - 0.4. A test using concentrated sludge (c = 0.11) with 55% excess acid after leaching gave an SFI of 34, and on briefly boiling the leach extract the SFI was reduced to about 0.70. The settling rate of the extracted sludge was also greatly improved by this heat treatment.

5.5 Preparation of Leach Liquor

Because the original sludge filter cake contained only about 19% solids, this placed a limit on the concentration of extract obtainable. If the reaction mixture is to be reasonably fluid, the maximum solids content of the reaction mixture can only be about 11%.

Concentrated sulphuric acid was added in 47.2% excess to filter cake with sufficient additional water to give a final slurry of 11% solids

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* See Figure 5 for the filterability defined here relative to fresh filter cake. Our "original" sample had about twice the specific resistance of fresh cake.

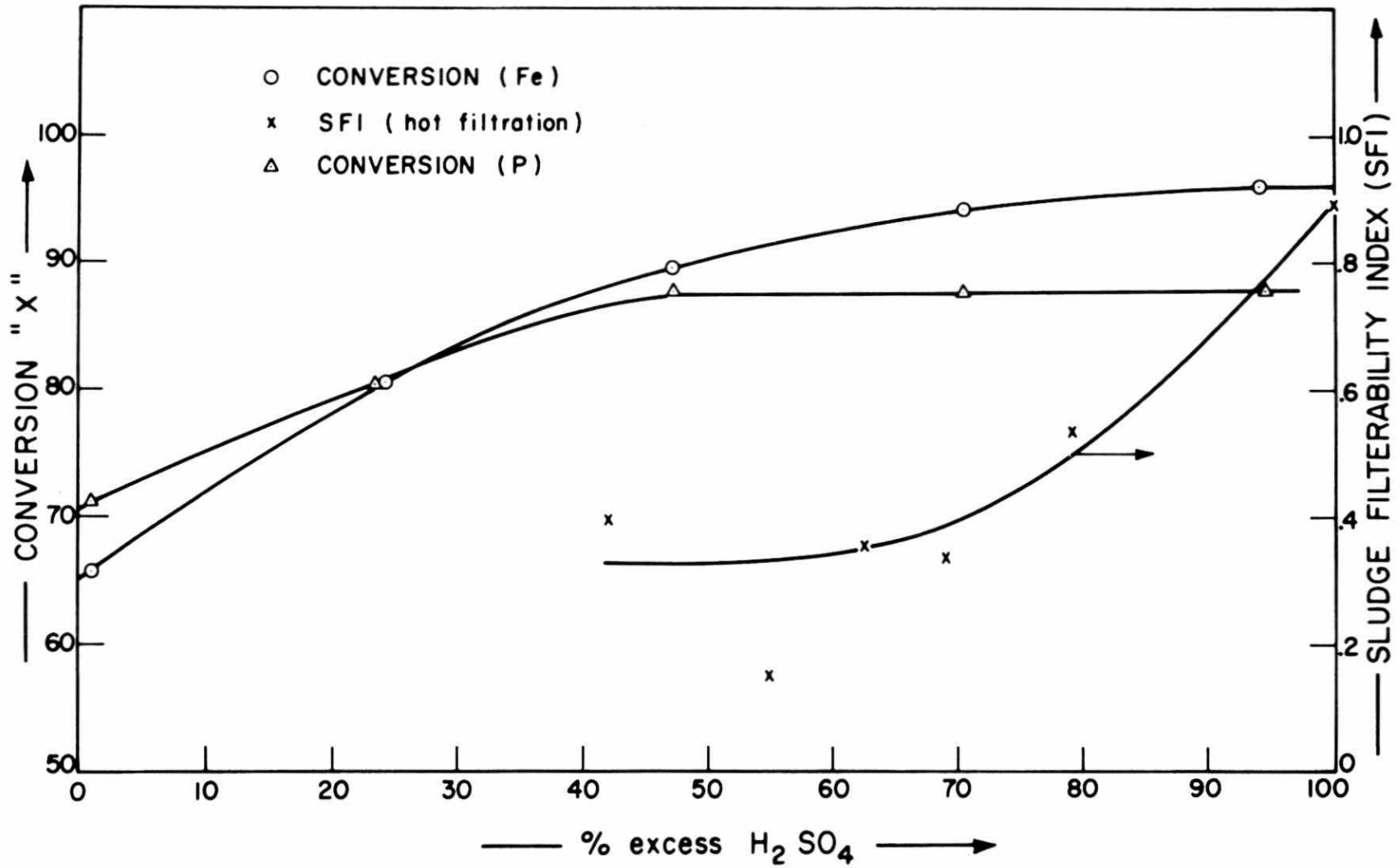

FIGURE 3. OPTIMIZATION OF EXCESS ACID IN EXTRACTION (H_2SO_4 with sludge sample equivalent to 20 gm dry solids, 1000 ml reaction mixture, 25.5°C; leaching time 15 min + 15 min heating.)

content*. Acid addition caused a temperature rise from 19°C to 40°C, and some initial gas evolution with consequent foaming in the early stages. After extraction for 15 minutes, the reaction mixture was heated to boiling, and then immediately filtered (SFI = 0.6 -0.7). After filtering, the residue from the extraction step retained a substantial fraction of the leach liquor. Therefore, displacement washing tests of the filter cake were carried out by collecting the displaced filtrate in fractions and analyzing it for iron content. Results of these tests are shown in Figure 4. About 85% of the extract liquor can be removed from the cake with the theoretical calculated displacement volume of washwater. Additional washing removes very little additional liquor. The moisture content of the washed cake was 59.5%, compared to 79% for the original cake.

The degree of extraction achieved was determined by taking a known volume of concentrated leach liquor, filtering off the leached boiled sludge, washing the cake, and then re-slurrying and filtering the cake twice. The original filtrate and the washings were combined and then analyzed. Results are given in Table 2.

TABLE 2. EXTRACTION YIELDS AND EXTRACT COMPOSITION

	Extract mg/gm dry solids	Original Analysis (C) mg/gm dry solids	Concentrated Leach Liquor gm/litre
Iron (Fe)	97	87.5	14.0
Phosphorus (P)	32.6	38.5	4.7
Calcium (Ca)	29.9	120	4.3
Zinc (Zn)	1.98	1.88	0.27
Copper (Cu)	0.97	0.98	0.14

The increase in iron content is due mainly to sludge sampling problems. Because of the method used in the treatment plant of adding ferric chloride and lime just prior to filtration, some non-uniformity of

* For example, 960 gm of wet filter cake "as is" were slurried with 800 ml of water. To the mixture 95 ml of concentrated sulphuric acid was slowly added to control foaming, zero time was taken as the beginning of acid addition.

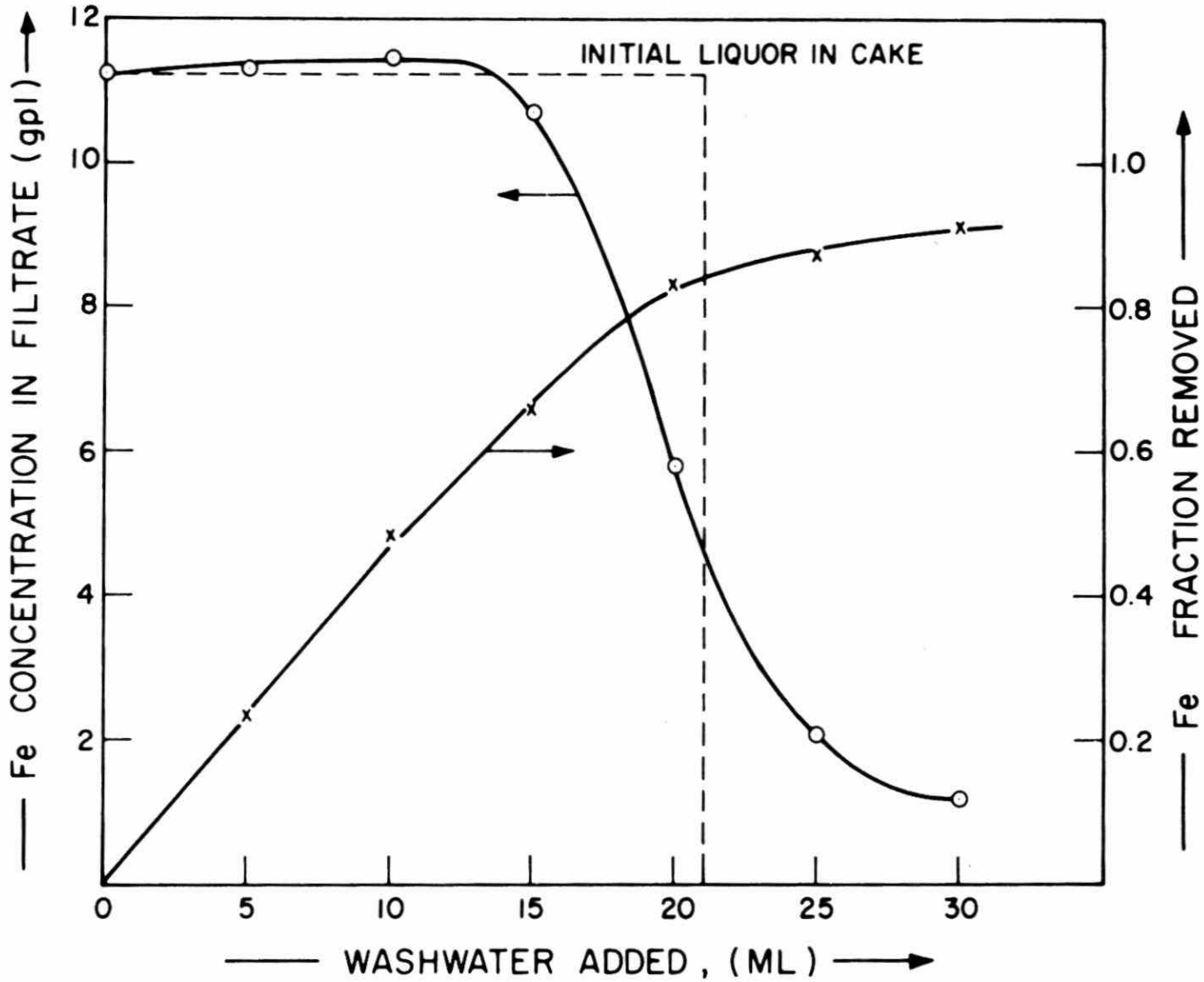

FIGURE 4. DISPLACEMENT WASHING OF EXTRACTED SLUDGE

iron content in the cake is to be expected. Although representative sampling was attempted from the bulk sample, apparently considerable effort is needed to obtain small reproducible samples. Calcium is somewhat variable, as the precipitation of $CaSO_4$ proceeds slowly, and solutions are not always at equilibrium.

As expected, essentially all metals having soluble sulphates are extracted nearly 100% by this procedure. The leach liquor is moderately dilute, and contains as soluble orthophosphate about 77 - 80% of the total phosphorus in the original influent to the treatment plant. The iron in the leach liquor is about one half in the ferrous form a result of the anaerobic treatment step in the plant.

5.6 Extraction Tests on Unconditioned Sludge

A sample of the underflow from the final digesters was obtained from the North Toronto Treatment Plant on January 10th, 1974, from a sampling valve in the filter feed line ahead of the feed conditioning tank. This sample was immediately taken to the laboratory and filterability tests were carried out on it within three hours of sampling. As expected the filterability of this unconditioned material was considerably poorer than that of the conditioned sludge.* The sludge filterability index, that is the ratio of specific filtration resistance of the unconditioned material to that of the conditioned material, was 75.

The detailed analysis of the metallic components of the digested sludge is given in Table 3. The pH of this sludge was rather high at 9.1, and it contained a significant amount of calcium.

It is worthwhile to compare the calcium content here, however, with that of the conditioned sludge which has nearly twice the lime content. An approximate evaluation of the costs of reagent for extraction of a conditioned sludge shows that the value of the sulphuric acid which must be used to solubilize over 90% of the iron and the phosphate represents a sum which is nearly equal to the ultimate value of iron and phosphate

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* A sample of conditioned sludge was also taken at this time and its filterability measured within three hours. The specific resistance of this material was taken as the base for defining sludge filterability indices in succeeding work. The effect of aging during storage on sludge filterability is shown in Figure 5.

TABLE 3. ANALYSIS OF DIGESTER UNDERFLOW

Sampled at North Toronto Plant of Metro Toronto

January 10, 1974

Moisture	93.0%	
% dry solids	7.0%	
pH	9.1	
Volatile Solids	3.23%	
		mg/gm dry sludge
Iron	Fe^{++}	75.0
	Fe^{+++}	0.0
Aluminum	Al^{+++}	7.8
Calcium	Ca^{++}	64.2
Zinc	Zn^{++}	2.87
Copper	Cu^{++}	1.23
Manganese	Mn^{++}	0.33
Chromium	Cr^{+++}	0.79
Phosphorus	P	37.4
Sludge Filterability Index		75

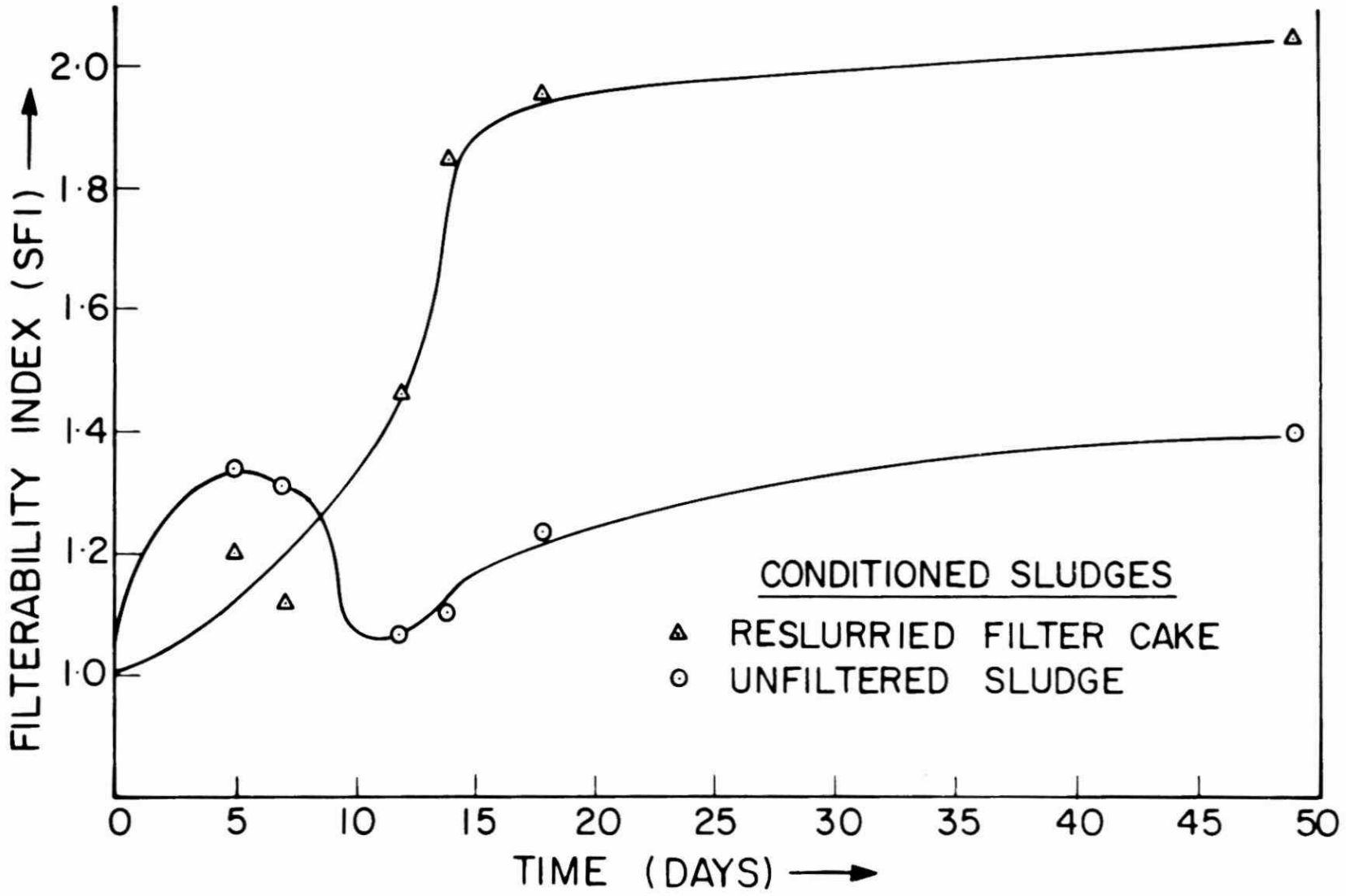

FIGURE 5. EFFECT OF STORAGE AT 0°C ON FILTERABILITY OF SLUDGE SAMPLES

which might be recovered in additional processing operations. It therefore became apparent that this consumption of reagent was more serious than the dilution of the extract which resulted from using the unconditioned digester underflow at 7% solids rather than a filter cake at 20% solids.

The results given in Table 3 were obtained by using hot digestion for two hours in concentrated hydrochloric acid. Apart from the decrease in calcium content of the sludge, the other noteworthy difference between this material and the conditioned sludge is the fact that all iron in the unconditioned sludge is in the ferrous form. It is obvious that ferric iron is present in the filter cake only because of the addition of ferric chloride for conditioning prior to filtration. It is interesting to note that the North Toronto plant consistently achieves greater than 90% removal of phosphate from the influent.

On the basis of the knowledge obtained from the extraction tests with the conditioned sludge, the unconditioned sludge was leached at only one set of conditions, that is, with 25% excess acid where the acid equivalent was calculated on the basis of the iron, zinc, calcium and aluminum contents. The sludge was extracted at its process concentration of 7% solids content by the addition of concentrated sulphuric acid, using the same methods as described earlier. The solubilization of phosphate and iron proceeded very rapidly at room temperature and reached maximum yield within fifteen minutes. On the initial addition of the acid a good deal of foaming occurred, equal in amount to approximately the volume of the original solution. This foam formation is probably due to the presence of carbonates in the sludge solids. The extract solution was tested for filterability after bringing the extract solution to the boiling point and filtering hot. Filterability was improved significantly over that of the original unconditioned sludge, but still not to the level of a properly conditioned sludge.

In Table 4 is shown the recovery of phosphate and iron in the extraction of the unconditioned sludge solids. It will be noted that the heating of the solution to boiling caused a small increase in yield, how-

TABLE 4. ACID EXTRACTION OF DIGESTER UNDERFLOW

	Extraction Conditions	Fe		P	
		gm /litre	% extracted	gm/litre	% extracted
1.	Hot boiling conc. HCl for 2 hours	5.40	100	2.67	100
2.	25°C, 25% excess H_2SO_4 15 min extraction time, no heating	5.03	93	2.35	88
3.	25°C, 25% excess H_2SO_4 15 min extraction time, followed by 15 min heating to boiling	5.35	99	2.42	90

ever, extraction was 85 to 90% even in the cold, and over 90% after heating.

Composition of the leach liquor obtained given in Table 5 shows some interesting differences from that reported in Table 2. No copper could be detected in the extract, whereas the extract from the filter cake contained all of the original copper.

TABLE 5. ANALYSIS OF EXTRACT FROM ACID LEACHING OF DIGESTER UNDERFLOW

25% excess H_2SO_4, 25°C, 15 min extraction time

Component	Concentration		
	gm/litre	mg/gm dry sludge	% Extracted
Fe^{++}	5.30	75.5	100
Al^{+++}	0.540	7.7	98
Ca^{++}	0.660	9.6	(*)
Zn^{++}	0.143	2.1	73
Cu^{++}	---	---	0
Mn^{++}	0.021	0.30	91
Cr^{+++}	0.030	0.43	54
P	2.575	36.8	98
Organic carbon	3.8	54.3	

Sludge Filterability Index 2.68 (after heating to boiling)

(*) Most of the calcium is precipitated as $CaSO_4$

6. SEPARATION OF METALS AND PHOSPHATES FROM EXTRACTS BY CHEMICAL MEANS

6.1 General

From observation of the extracts obtained both from the conditioned sludge filter cake and from the digester underflow, it was apparent that a good deal of acid-soluble organic material was present. Extract solutions were also dark in colour. If solvent extraction was used directly with this extract, much of the dissolved organic material could be expected to transfer to the organic phase, leading to contaminated solvents and a need for excessive solvent reclamation. For this reason, an additional purification step was thought to be desirable, primarily to separate the metallic cations and the orthophosphate from the water soluble organic material.

Since the metals all form insoluble phosphates and insoluble hydroxides in neutral or alkaline solutions, this presented a simple technique of separation. An attempt was made to obtain solubility product data for the possible hydroxides and orthophosphates that would be formed (Table 6). These data can be used only as an approximate guide, inasmuch as the exact nature of solid precipitates formed with phosphate at various pH values is not definitely known for many of these cations. In addition to solubility product data and data on stability constants, some experimental work has been reported in the literature, notably that of Recht and Ghassemi (11) on aluminum and ferric phosphates, and Ghassemi and Recht (6) and Singer (15) on ferrous phosphates. Most of the experimental work has been carried out in very dilute solutions, typical of concentrations found in wastewater treatment plants. In the extracts prepared here, the solutions are only moderately dilute, and are of the order of more than a hundred times more concentrated than normal wastewaters. Therefore, precipitation reactions should occur completely and rapidly.

The experimental studies mentioned indicate that ferric iron orthophosphate compounds begin to precipitate at pH values above 2.0 and the optimum range for precipitation is at pH 3.5 - 4.0. Aluminum orthophosphate compounds precipitate initially at a pH of 2.5 - 3.0 and the optimum pH is in a range of 4.0 - 6.0. Ferrous ion appears to

TABLE 6. SOLUBILITY PRODUCTS AND EQUILIBRIUM CONSTANTS

Sources: Sillen and Martel (13)
Singer (14)
Singer (15)

Solubility Products for Hydroxides $M(OH)_y = M^{y+} + yOH^-$

$Al(OH)_3$	$K_{so} = 10^{-31.7}$
$Fe(OH)_3$	$K_{so} = 10^{-38}$
$Fe(OH)_2$	$K_{so} = 10^{-13.8}$
$Zn(OH)_2$	$K_{so} = 10^{-17}$
$Cu(OH)_2$	$K_{so} = 10^{-19.7}$
$Cr(OH)_3$	$K_{so} = 10^{-30}$
$Mn(OH)_2$	$K_{so} = 10^{-13}$
$Ca(OH)_2$	$K_{so} = 10^{-5.3}$

Solubility Products of Orthophosphates

$AlPO_4$ - Probably does not exist in aqueous solution

$Al(H_2PO_4)(OH)_2$ - Possible solid compound, $K_{so} = 10^{-30.5}$

$FePO_4$ $K_{so} = 10^{-24}$ (Probably not formed in aqueous solution)

$Fe(H_2PO_4)(OH)_2$ - Possible form, $K_{so} \approx 10^{-34}$

Many other polynuclear compounds reported formed as precipitates in aqueous solution.

$Fe_3(PO_4)_2$	$K_{so} = 1.3 \times 10^{-30}$
$Zn_3(PO_4)_2$	$K_{so} = 10^{-32.04}$
$Mn_3(PO_4)_2$	No evidence of existence in solution
$Cu_3(PO_4)_2$	$K_{so} = 10^{-36.9}$
$CrPO_4$	$K_{so} = 10^{-22.6}$
	(Many other more likely possibilities)
$Ca(H_2PO_4)_2$	$K_{so} = 10^{-1.14}$

(cont'd)

TABLE 6. (CONT'D)

$Ca\ HPO_4 \cdot 2H_2O$	$K_{so} = 10^{-6.57}$
$Ca_5(OH)(PO_4)_3$	$K_{so} \approx 10^{-44.6}$
$Ca_3(PO_4)_2$	$K_{so} \approx 10^{-28.7}$

precipitate as a stoichiometric ferrous phosphate with orthophosphate. Precipitate of this compound appears at a pH of 6.0 and the optimum pH is around a value of 8.0. For all three cations as the pH increases above 9 the orthophosphate becomes solubilized again.

Pascal (9) has reported that when orthophosphate is added to a zinc salt in solution at a concentration of 0.1 N, precipitation of a zinc phosphate ($Zn_3 (PO_4)_2$) begins at pH 5.6. Similar data on copper, manganese or chromium phosphates may be available, but no exhaustive search for this information was carried out because of the small amounts of these constituents in the extract. Calcium orthophosphate chemistry is complicated, and mixtures of phosphates are usually obtained in precipitates. However, according to Van Wazer (19), when calcium is added to a solution containing orthophosphate the first solids to appear, as pH is increased, is monocalcium phosphate, ($Ca(H_2PO_4)2$, at a pH from 4.0 - 4.5. As further calcium is added up to one equivalent, pH tends to decrease and mixed phosphates are precipitated, for example, $CaHPO_4$ and hydroxyapatites [sometimes given the formula $Ca_5 (OH)(PO_4)_3$].

6.2 Purification by Precipitation of Extract from Filter Cake

A number of liquids from different extractions were combined to give a sufficiently large quantity of extract solution for precipitation tests. The composition of this combined extract, all of which was prepared from the same sample of filter cake as used in previous tests, is given in Table 7.

A sample of the extract was placed in a beaker and pH was measured continuously while sodium hydroxide solution was added until the pH had reached a predetermined value. As precipitation occurred, the pH tended to decrease and therefore sodium hydroxide was added continuously with stirring until the pH became constant. This usually occurred in less than 20 minutes and in all cases was complete in under 30 minutes. At the end of this period, when the pH had been constant for several minutes, the solution was filtered and a sample of the filtrate was analyzed for various cations or anions. The results of these tests, showing the residual fraction of the cation or anion still remaining in the extract as a function of the pH of the extract, are shown in Figure 6. In accordance

TABLE 7. COMPOSITION OF COMBINED EXTRACTS FROM ACID EXTRACTION OF FILTER CAKE

Constituent	Initial Concentration (gm/litre)
Iron, ferric	4.16
Iron, ferrous	6.64
Aluminum	1.20
Calcium	1.63
Zinc	0.25
Copper	0.125
Chromium	0.060
Phosphorus	4.50
Total Carbon	6.0
pH	0.7

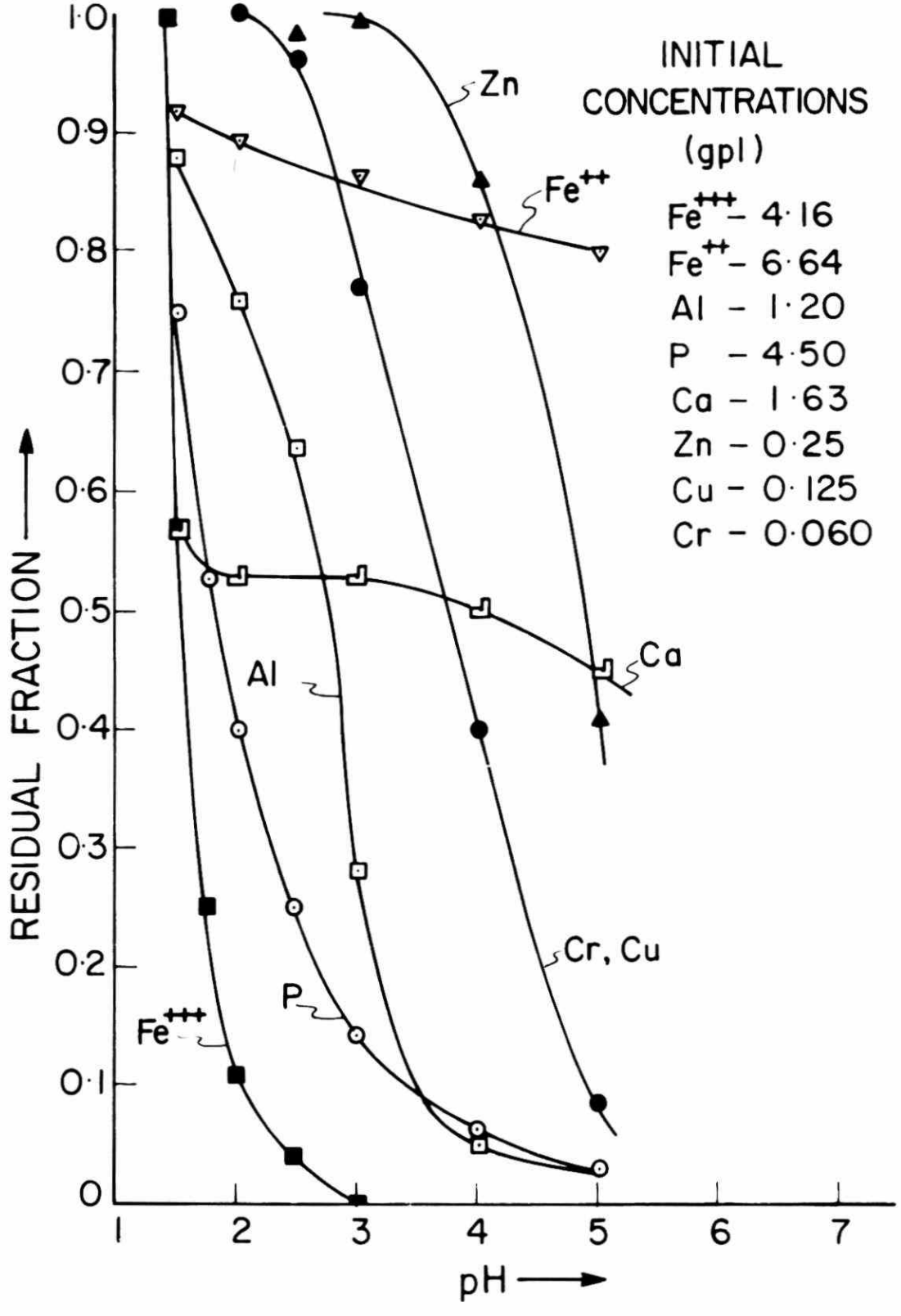

FIGURE 6. PRECIPITATION OF METALS AND PHOSPHATE FROM EXTRACT SOLUTION - CONDITIONED FILTER CAKE

with the approximate predictions from solubility data, the first precipitate to form is the ferric salt, presumably a hydrated phosphate complex. Inasmuch as the mol ratio of ferric/phosphate is less than one, probably not all the phosphate will combine with ferric ion even if the precipitate is a hydrated ferric phosphate compound. See Recht and Ghassemi (11). Precipitation of the ferric orthophosphate complex begins at a pH of 1.5 and virtually all the ferric ion has been removed by the time the pH has been increased to 2.5. Precipitation of the aluminum phosphate complexes begins also at about pH 1.5, but from the results shown in Figure 6, it appears that the formation of the ferric complex is favoured slightly and the aluminum complex formation does not proceed rapidly until most of the ferric ion is depleted. Again this is in agreement with previous experimental results obtained by others (11). By the time the pH has risen to 3 all the ferric ion and most of the aluminum has been precipitated and has removed about 90% of the phosphate in solution.

At pH 3 copper and chromium also begin to precipitate and by the time the pH is equal to 5, essentially all of these materials have been removed from solution. From a pH of 4 to 5 most of the zinc is precipitated but very little ferrous iron has been removed, even at a pH of 5. The behaviour of calcium is interesting. About one half of the calcium is removed immediately the pH is increased from its original value 0.7 to 1.5 and then very little additional calcium precipitates as the pH is increased to 5. The first formation of monocalcium phosphate, as discussed earlier, is supposed to take place at a pH above 4, and it would appear that this initial precipitation of calcium at lower pH is not likely to be in the form of a calcium phosphate. There is a relatively small amount of calcium in solution and an examination of solubility data indicates that as the pH is raised, the solubility of calcium sulphate decreases by about 25%. It is likely, therefore, that this initial decrease in calcium content of the filtrate over a pH range of 1.5 - 3.0 is due primarily to a change in solubility of the dissolved calcium sulphate.

An examination of the results suggests that when ferric iron is present in the majority, it would be possible by adjusting the pH of an extract to 3 to remove essentially all the ferric iron, most of the

aluminum and all of the orthophosphate, and leave in the solution the bulk of the heavier metals such as copper, chromium, zinc, as well as any ferrous iron. While this approach to a separation is of doubtful value for the present extract because the bulk of the iron is, in fact, in the ferrous form, it could well be a very useful approach for sludges which have not undergone anaerobic digestion. In these sludges it would be expected that the iron would be primarily in the ferric form. Similarly, it may be that sludges in which alum has been used for phosphate removal, whether they have been anaerobically digested or not, may well be suitable for treatment by this type of selective precipitation.

In this work sodium hydroxide was used in order to adjust the pH of the extract. There is no necessity to use sodium hydroxide, which is a relatively expensive chemical, as the pH adjustment could have been carried out as successfully using lime. However, in this case, a rather more voluminous precipitate would be obtained because additional quantities of calcium sulphate would precipitate, but this would present no particular problem when carrying out a selective precipitation. The calcium sulphate formed is not soluble in moderately acid or alkaline solutions, and thus it should be possible to separate iron and aluminum, or phosphate, from the calcium sulphate residue by dissolving them in either acid or alkali, respectively.

The precipitates obtained contained a good deal of metallic hydroxides as well as phosphates, and were fairly flocculent in nature. They did not filter particularly well, but presumably standard techniques could be applied in order to improve the filtration rates of these hydroxide or phosphate compounds. If a selective precipitation at a pH of 3 were carried out in the case of sludges containing primarily ferric or aluminum ions, then the filtrate from this step would contain 80% or more of the heavy metals and most of the ferrous iron, as well as the dissolved organic impurities. This filtrate could then be disposed of separately as a noxious stream, probably by raising its pH further and precipitating all of the heavy metals as their hydroxides, filtering them off, and discarding this cake separately from the filtrate which could be returned to the normal effluent disposal streams. While the filter cake containing the heavy metals probably has a significant commercial value

per pound, the very small quantity of it would not likely make it worthwhile to consider it as a commercially useful source of heavy metals.

6.3 Purification by Precipitation of Extract from Digester Underflow Sludge

The composition of the extract used has already been given in Table 5. Because less excess acid was used in this case, the initial pH of this extract was 1.5 as compared to a pH of 0.7 for the extract prepared from the conditioned filter cake solids. The procedure for carrying out the precipitation from these extracts was essentially the same as for the filter cake extracts, and the results obtained are again predictable from the known solubility data. These results are shown in Figure 7 for the principal cations in the mixture

The principal difference between this extract and the previous one is the complete absence of ferric iron, and the generally lower iron content of the solution. As pointed out earlier, ferrous iron has been reported to combine with orthophosphate to form a fairly well defined ferrous phosphate compound (6) which does not begin to precipitate until the pH is of the order of 5 or greater. As can be seen in Figure 6 the phosphate removal curve initially drops off between a pH of 2 and 3 due to the precipitation of the aluminum phosphate compounds, and somewhat more slowly between pH 3.5 - 4.5, presumably because of the precipitation of the small amount of zinc and minor amounts of other heavy metals.

From the analysis of the leach liquor given, it is apparent that even allowing for the formation of aluminum phosphate and corresponding orthophosphate compounds with other cations, there is not enough calcium, aluminum, zinc, chromium and manganese combined to remove more than about one half the total orthophosphate in the solution. In Figure 7 it can be seen that there is an inflection point in the phosphate removal curve at a pH of a little over 4 when about 45% of the phosphate has been removed. Indeed at a pH of 5, one can safely assume that all of the heavy metals, including the zinc, are precipitated either as phosphates or hydroxides and that only a minority of the ferrous iron has yet been removed from the extract. Above a pH of 4.5 the removal rate of orthophosphate parallels the reduction in ferrous ion content of the

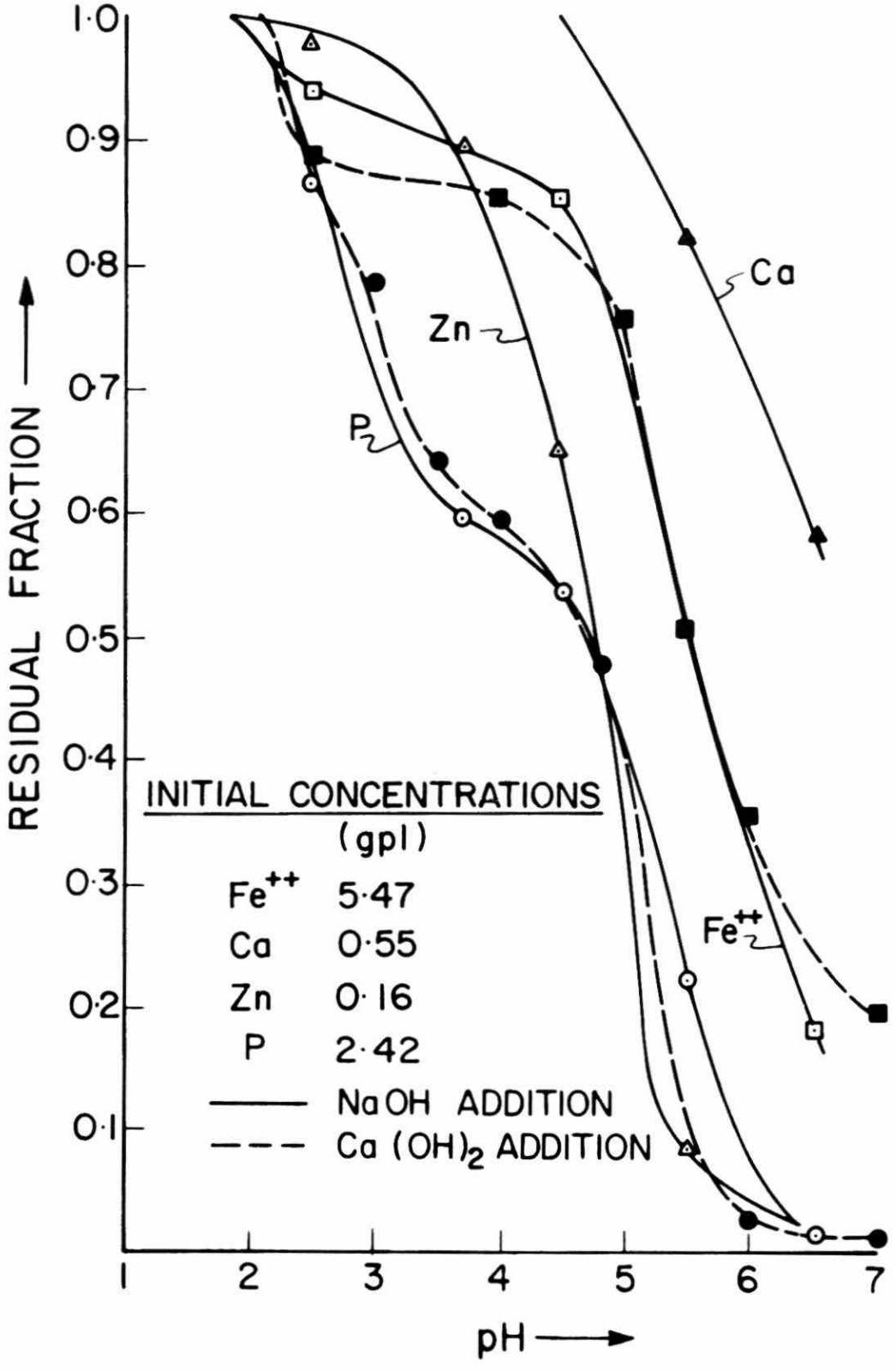

FIGURE 7. PRECIPITATION OF METALS AND PHOSPHATES FROM EXTRACT SOLUTION - UNCONDITIONED SLUDGE UNDERFLOW

solution. In the region from 50% to 5% residual phosphate the results correspond to a removal rate of ferrous ion in the molar ratio of 1.5 ferrous to 1 of orthophosphate, as would be required by the formation of ferrous orthophosphate. From the composition of the extract shown in Table 5, it can be found that the amount of ferrous ion is just about sufficient to precipitate the remainder of the phosphate in the solution, after the solution has been brought to a pH of 4.5. Hence, by the time the pH has been raised to 7, the phosphate has fallen virtually to zero and the ferrous iron is almost completely removed from the solution.

At pH 5.6 a small amount of calcium phosphate compound begins to form and precipitates until essentially all the phosphate has been removed from solution.

The possible application of fractional precipitation is not quite so promising in the case of this extract as for the previous extract. If the pH of the extract were adjusted to 4.5, then the resulting precipitate would contain essentially all the heavy metal ions, a small proportion of the ferrous iron and about one half the phosphate in the solution. It would be possible to dispose of this cake separately after filtering, particularly as the quantity is small. The filtrate would contain the remainder of the orthophosphate, most of the ferrous iron and most of the calcium, as well as the dissolved organic materials and other soluble anions and cations. A precipitate consisting primarily of ferrous phosphate, together with some calcium phosphate, could be obtained by further raising the pH to about 7. Alternately, the entire extract can be brought to a pH of 7 and the resulting solids can be filtered off and then considered as a raw material from which phosphate and ferrous iron might be extracted for possible reuse or recycling. This alternative has the advantage that all of the phosphate would then be available for recovery rather than only about one half of it. Inasmuch as the phosphate is present in significant amounts and has a nuisance factor if disposed of on a land site and has a commercial value if recovered, it would be desirable not to reject the bulk of the phosphate in a solid waste material at this point. Therefore, it was this alternative which was selected for further study in this work. However, if a sludge under consideration contained relatively low amounts of heavy metal ions, then loss of

phosphate in this precipitate would not be large and it might be entirely feasible to dispose of the heavy metals by a fractional precipitation procedure.

The large sample of the extract was adjusted to a pH of 7, held there until the pH was constant, signifying completion of the precipitation reactions, and the precipitate was then filtered, dried at 100°C and analyzed. The filtrate from this precipitation step was also analyzed in order to check the distribution of the various constituents between the two fractions. The results of analyses on the filtrate and the precipitate are given in Table 8. With the exception of the calcium, all analyses of major components check out with the amount originally present in the extract. From the analysis of the dry cake, it can be seen that the cake is about 70% ferrous phosphate by weight, and contains about 90% of the ferrous iron originally in the extract and about 97% of the phosphorus originally present in the extract. The filtrate from this step is a relatively innocuous material containing only dissolved organics, soluble cations and anions such as sodium, potassium, sulphate, chloride, etc. and only a small amount of ferrous ion or phosphate and practically no heavy metals. This material then could be returned to the effluent streams of a treatment plant with no problem.

In preparing the cake having the analysis given in Table 8, sodium hydroxide was used for convenience in adjusting the pH to a value of 7. However, lime could also be used, and the resulting large amounts of calcium sulphate formed might improve the filterability of the cake. Further precipitation tests were, therefore, carried out using the same procedure already described, but with pH adjustment done by addition of 0.04 N $Ca(OH)_2$ to the extract, the analysis of which is given in Table 5. The variation of the concentrations of ferrous iron and phosphate, as pH was increased, is shown as dashed lines in Figure 7. It is apparent from the similarity of the results that the nature of the metallic precipitates are virtually the same regardless of whether NaOH or Ca(OH)2 is added.

In the results shown in Table 8, the iron is reported as ferric iron. When this cake is filtered at a pH of 7 and the organic materials are removed after washing the cake, oxidation of the ferrous material

TABLE 8. PRECIPITATION OF METALS FROM EXTRACT FROM DIGESTER UNDERFLOW SOLIDS

Temperature 25°C, Final pH = 7.0

pH adjustment using NaOH

Analysis of Precipitate

Constituent	Concentration		% Recovery	
	mg/gm of dry cake	mg/gm dry sludge	Sludge	Extract
Iron Fe^{+++}	266.0	68.5	91	90
Aluminum Al^{+++}	25.6	6.6	84	85
Zinc Zn^{++}	7.8	2.0	69	95
Calcium Ca^{++}	19.0	4.9	7	51
Manganese Mn^{++}	0.91	0.23	69	76
Chromium Cr^{+++}	1.32	0.34	43	79
Copper Cu^{++}	Nil	Nil	Nil	Nil
Phosphorus P	140	35.9	96	97
Organic C	3.4	0.8-1		

Analysis of Filtrate

	gm/litre	mg/gm dry sludge	%
Iron Fe^{++}	0.48	6.90	9
Zinc Zn^{++}	0.001	0.03	1
Manganese Mn^{++}	.004	0.11	33
Cr^{+++}, Cu^{++}, Al^{+++}	0	0	Nil
Phosphorus	0.006	0.17	0

occurs very rapidly in the air and the precipitate rapidly assumes the normal brownish ferric colour.

6.4 Oxidation of Ferrous to Ferric Iron in Sludge and Extract Solutions

It is apparent from the precipitation results given in Figure 7 that the removal and separation of phosphate and metal ions is simplified if the iron is present either entirely in the ferric form or entirely in the ferrous form. In the case of the conditioned sludge filter cake, there were roughly equal amounts of ferrous and ferric iron present. An attempt was made to oxidize the filter cake before acid extraction in order to convert all the iron to the ferric form. This was done by slurrying a sample of the conditioned filter cake, adjusting the pH to between 9 and 10 and then heating it to 170°F and aerating it for one hour. No measurable oxidation was found to occur in this period. A similar test was done using a sample "as taken" of the unconditioned digester underflow, which has a pH of 9.1. This sample was also held at 170°F for one hour while being vigorously aerated and again no measurable oxidation of ferrous to ferric iron occurred. These results are in agreement with results reported by Singer and Theis (16) who suggested that times of three hours or more were needed in order to oxidize a reasonable proportion of the ferrous iron to ferric iron in the presence of organic compounds. On the other hand, a sample of the filter cake consisting largely of ferrous phosphate, which was prepared from the extract from the underflow solids, was reslurried and adjusted to a pH of 10.7. It was then aerated at room temperature and in less than 15 minutes, all the ferrous iron had been coverted to the ferric form. Again this result is in agreement with the work of Singer and others, as reported by Singer (14), who pointed out that in the absence of organic compounds, the oxidation of ferrous iron proceeds very rapidly when the pH is greater than 7.

7. USE OF SOLVENT EXTRACTION FOR RECOVERY OF METALS AND PHOSPHATES FROM ACID EXTRACTS

Two approaches were used in evaluating the potential of solvent extraction techniques. Phosphoric acid is presently recovered industrially by solvent extraction techniques from phosphate containing hydrochloric acid solutions. These methods are essentially separations between hydrogen ions and metallic cations and are not selective for the phosphate ion. It was felt that, given analyses of typical feed materials to be subjected to solvent extraction, it would be possible to arrive at conclusions concerning the potential usefulness of the technique on the basis of published information and known technology.

A second approach lay in the possibility of phosphate extraction by the use of phosphate - specific complexes. The most promising of these is a group of tin-organic ligand complexes. One investigation has been reported concerning the potential usefulness of these compounds for extracting phosphate from very dilute solutions (5).

7.1 Use of Triphenyl Tin Compounds for Phosphate Extraction

Distribution coefficients for various anions between benzene solutions and aqueous solutions has been given for a variety of triphenyl tin complexes in two papers by Bock and co-workers (2,3). From these results, it appeared that triphenyl tin compounds might be useful for the separation of anions. These compounds specifically extract phosphate from aqueous solutions at low pH in the presence of sulphate ion, and the phosphate can be readily removed by stripping at high pH with dilute sodium hydroxide.

Triphenyl tin has not been seriously investigated previously as a commercial reagent for solvent extraction of phosphate, having been discarded as "too expensive" and "too unstable" by previous reviewers (8). In fact, triphenyl tin salts are stable at room temperature in moderately strong acid or alkaline solutions. They are decomposed by strong acids or alkalies or by strong oxidizing agents (3).

The properties of triphenyl tin hydroxide appeared to hold some promise for its use as an extraction agent. This compound acts as a liquid anion exchanger, and will extract phosphate preferentially from

acid solution. The reaction is easily reversed, and the triphenyl tin hydroxide can be regenerated by exchange with dilute sodium hydroxide. It has been claimed (2), that the reactions are nearly quantitative. Sulphate ion is not extracted, although halogens, nitrates and some other anions are extracted under the same conditions as phosphates. The net reactions may be written for the orthophosphate ion as

(1) $3(C_6H_5)_3\ Sn\ OH + PO_4^{3-} \rightarrow [(C_6H_5)_3\ Sn]_3\ PO_4 + 3OH^-$

(2) $[(C_6H_5)_3\ Sn]_3\ PO_4 + 3NaOH \rightarrow 3(C_6H_5)_3\ Sn\ OH + 3Na^+ + PO_4^{3-}$

The triphenyl tin hydroxide is in equilibrium with its anhydride in numerous organic solvents according to the reaction

$$2(C_6H_5)_3\ Sn\ OH \rightleftarrows (C_6H_5)_3\ Sn.O.Sn\ (C_6H_5)_3 + H_2O$$

However, this equilibrium is established so quickly that a solution of the hydroxide in contact with an aqueous phase behaves as if it were entirely in the hydroxide form.

The distribution of triphenyl tin hydroxide between aqueous and organic layers is shown in Figure 8, for equal volumes of the two phases, with the organic phase containing originally 13.3 millimoles/litre of the hydroxide. Providing the pH is above about 2.6, the tin compound remains almost entirely in the organic phase.

The distribution of phosphoric acid between the aqueous and organic phases is shown in Figure 9 for equal volumes of phases, with originally 13.3 m. moles/litre of triphenyl tin hydroxide in benzene in the organic layer, and 6.7 milli equivalents/litre of phosphoric acid in the aqueous layer. A maximum of about 94% of the phosphate can be extracted from the aqueous phase in one stage under these conditions, at the optimum pH of 2.0 - 2.5. The phosphate can be transferred quantitatively from the organic phase to the aqueous phase by contact with dilute (e.g. 0.1 N) sodium hydroxide.

From these data, there appeared to be a reasonable likelihood of achieving a workable process using triphenyl tin hydroxide. Reagent losses could be held to a minimum, since any of the tin compound lost in aqueous raffinates can be easily recovered by stripping with fresh solvent

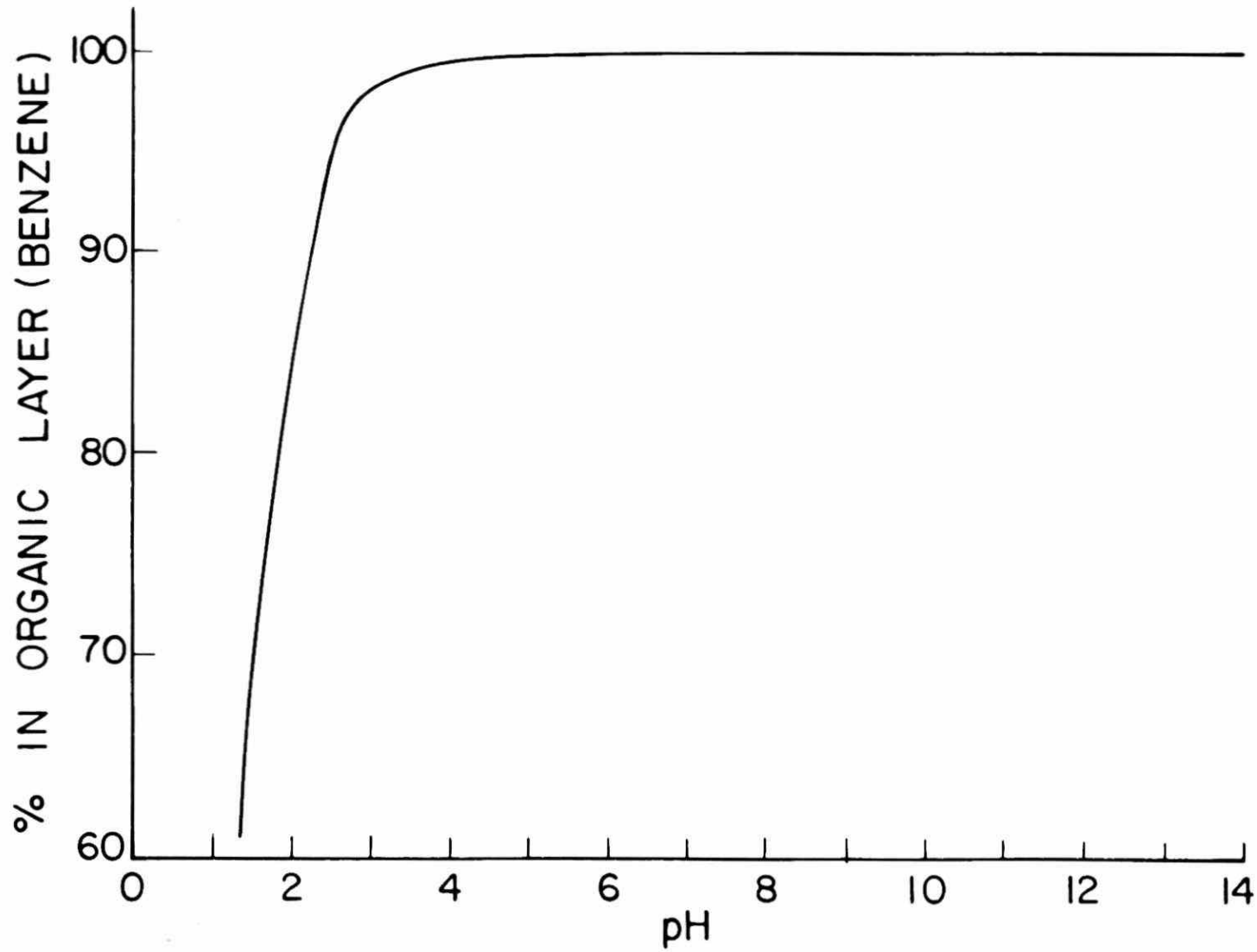

FIGURE 8. DISTRIBUTION OF TRIPHENYL TIN HYDROXIDE. BETWEEN WATER AND BENZENE

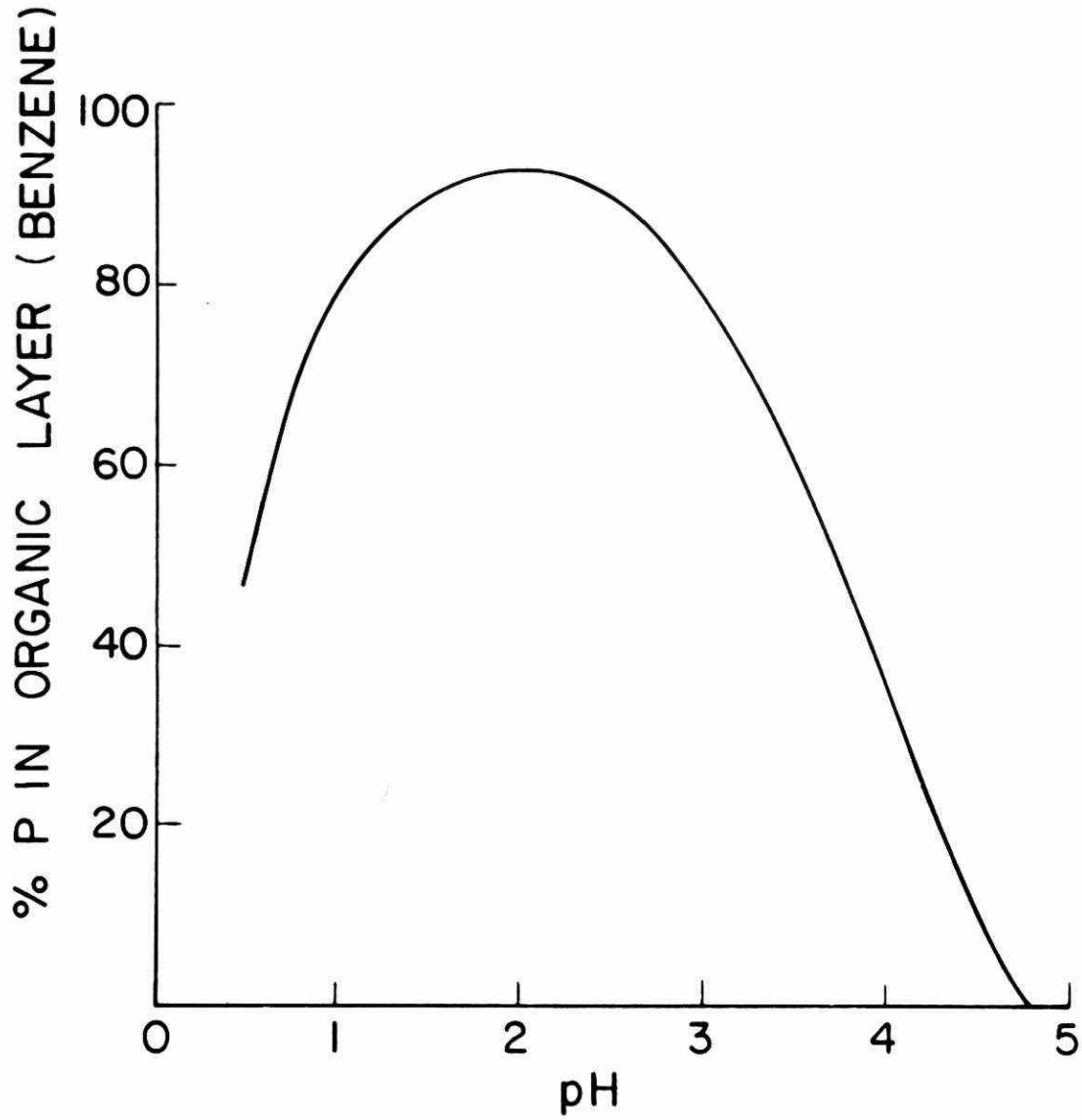

FIGURE 9. DISTRIBUTION OF PHOSPHATE BETWEEN WATER AND BENZENE CONTAINING TRIPHENYL TIN HYDROXIDE.

at any pH above 7.0. Although the cost of triphenyl tin compounds for laboratory use is presently high, these chemicals are employed presently in Europe as a fungicide, and hence production on a commercial scale is already taking place. While their toxicity has not been extensively investigated, this factor does not appear to be of major concern.

7.2 Experiments with Triphenyl Tin Hydroxide

A search of the literature was made in an effort to determine the solubility of triphenyl tin hydroxides, phosphates, chlorides etc. in water or organic solvents. Only qualitative information was obtained, although one value found for the solubility of triphenyl tin in benzene did not suggest that the salts of triphenyl tin would be highly soluble.

Solubilities were measured for triphenyl tin hydroxide (Alfa Inorganics) at room temperature in benzene, toluene, methyl isobutyl ketone, n-decyl alcohol and n-octyl alcohol. Solubility values obtained are listed below for each solvent.

	Solubility, moles/litre
Benzene	0.071
Toluene	0.0775
Methyl Isobutyl Ketone	0.0515
N-decyl alcohol	low
N-octyl alcohol	very low

From the above results, toluene was chosen as the preferred solvent, because it shows both the highest solubility for triphenyl tin hydroxide as well as the lowest miscibility with water.

The low solubility means that large volumes of organic phase are required to extract a reasonable amount of phosphate. For example, acid extract solutions from sludges contain from 0.08 - 0.15 moles/litre of phosphate. Even using saturated solutions as the organic phase, organic to aqueous phase volume ratios would range from 4 to 6. If the extraction procedure is carried out on an aqueous solution prepared from precipitated cake, much higher phosphate concentrations can be realized. However, low aqueous volume minimizes the loss of tin compounds in the stripped aqueous raffinate.

The precipitate obtained from the extract prepared from conditioned sludge filter cake was used as the source of phosphate. Precipitation was carried out to a pH of 4.5. The amounts of some major constituents of this cake were:

Phosphorus (as $PO_4^{\equiv}$)	49.0 weight %
Ferric iron	18.1
Ferrous iron	1.2
Aluminum	4.5
Organic C	0.4

This cake is completely soluble in acid solutions having a pH below 1.5. However, this is below the optimum region for phosphate extraction, and at this pH a considerable fraction of the triphenyl tin hydroxide also will dissolve in the aqueous phase. Therefore, a quantity of precipitate was slurried with 50 ml of water, such that the total phosphate content was 3×10^{-3} moles of $PO_4^{\equiv}$ (not all in solution) and the pH was adjusted to 2.0. At this pH, some phosphate was still not in solution. To simulate the results of multi-stage extraction, this aqueous mixture was to be extracted six times with an equal volume (50 ml) of a toluene solution of triphenyl tin hydroxide, containing 1.5×10^{-3} moles of tin compound in each 50 ml portion.

The aqueous and organic phases were mixed, thoroughly agitated and then allowed to separate. During the extraction of phosphate the pH of the aqueous phase increased due to the hydroxyl ions introduced, and so the pH was adjusted after an extraction step to restore the pH to 2.0. The two phases did not separate easily and cleanly. On separating, a considerable amount of solid appeared at the interface in the organic layer. After the first extraction, a sample of the organic layer was taken, the phosphate extracted by contact with 0.2 N sodium hydroxide, and the resulting aqueous solution was analyzed for phosphate. From the analysis it was concluded that phosphate equivalent to 67% of the original triphenyl tin hydroxide was present in solution, that is about 0.3×10^{-3} moles of PO_4. Presumably the balance of the phosphate equivalent to the triphenyl tin hydroxide appeared as a portion of the solid formed, although this solid material was not analyzed. However, these results suggest that the solubility of the triphenyl tin - orthophosphate complex in

toluene is only of the order of 0.0067 moles/litre.

A second 50 ml portion of solvent was used to contact the original aqueous solution, plus the solid formed, after adjusting the pH to 2.0. After shaking, a poor separation was again obtained, and solid precipitates appeared in both organic and aqueous phases. On analysis, very little soluble phosphate was found in the organic layer.

In view of the apparent very limited solubility in water or toluene of the triphenyl tin - orthophosphate compounds formed, these experiments were terminated. While there is adequate evidence in the literature that phosphate ion can be extracted and recovered readily and nearly quantitatively from dilute aqueous solutions using triphenyl tin hydroxide, the difficulties of using very dilute solutions, and the costs of reagents, suggests that better ways are probably available for the separation or recovery of phosphate from sludge extracts.

7.3 Conventional Solvent Extraction Techniques

In applying known solvent extraction technology to the separation of metals and phosphate from a cake having a composition similar to those obtained in this work, the two outstanding characteristics to be considered are the stability of iron-phosphate complexes in aqueous systems over wide ranges of pH, and the lack of specifically acting solvents for the phosphate anion.

In order to easily remove iron from phosphate, a strongly acidic solution is probably best. Extraction of iron with tributyl phosphate (TBP) from strong solutions of HCl is presently practiced (18). Some phosphoric and hydrochloric acid will probably be extracted also along with the iron by the TBP (12), and a scrubbing step for the organic phase using acidic ferric chloride solution might be necessary, with the ferric chloride recycling to the original feed. The TBP can be easily stripped with water, and a weakly acidic solution of ferric chloride is the product.

Other solvents which can extract ferrous or ferric ions have been reported. For example, a tertiary amine (Alamine 336) has been claimed as an extractant for ferric ions from highly acidic solutions. Di-2-ethylhexyl phosphoric acid and carboxylic acid have also been tested but do not seem to be as advantageous as TBP or tertiary amines for iron extraction.

Once the iron has been removed, the strongly acidic solution can be treated for phosphate removal by the TMT process (7). In this process, phosphoric and hydrochloric acid are extracted together into an alcohol (isoamyl alcohol or n-butanol). The organic phase can be water stripped to give a solution of acids and a good deal of solvent. The solvent can be recovered by a steam stripping operation, and the hydrochloric and phosphoric acids separated by distillation. The hydrochloric acid is returned to the cake dissolution stage. The stripped solvent returns to the extractor, sometimes contacting the original raffinate first. The aqueous raffinate is finally steam stripped to recover solvent and hydrochloric acid, and then forms a product stream containing most of the metal ions as chlorides but essentially free of acid or iron.

A possible flowsheet is given in Figure 10 to show the processing steps necessary. Some experimentation would be necessary, particularly to determine the best operating conditions for the TBP extraction of iron, and to check on solvent and acid losses in the various streams from the phosphate extraction step. In principle, as can be seen from the flow sheet, all reagents are recovered and recycled.

In summary, then, the following process would seem to be technically feasible.

1. The cake from a selective precipitation is dissolved in HCl and the iron extracted with TBP or a tertiary amine. The TBP or amine can then be treated with water to recover the iron as ferric chloride.
2. The phosphoric and hydrochloric acid can be extracted from the raffinate from the iron extraction step using an alcohol. The alcohol is stripped with water to recover the acids which are then separated by distillation and the HCl is recycled. Only make-up reagents are required, and treatment costs should be limited to these costs plus other process operating costs and the amortization costs.

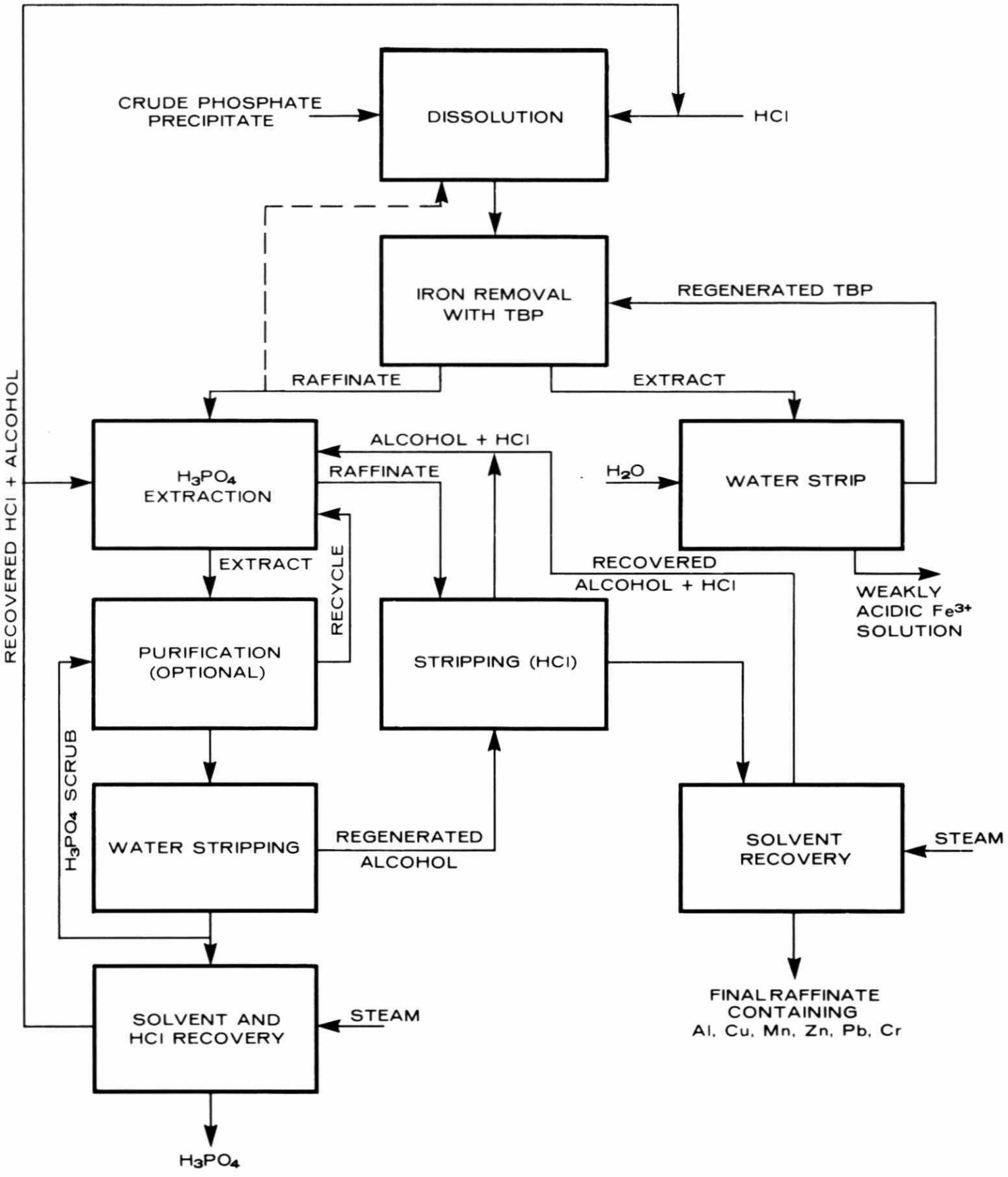

Figure 10 Suggested Flowsheet for Iron and Phosphate Extraction by Conventional Solvent Extraction

8. SEPARATION OF PHOSPHATES

Given a solid product filter cake of the approximate composition shown in Table 8, it would be desirable at least to separate the orthophosphate and the iron, so that they can be disposed of or re-used separately, as the case may be.

Two approaches for this separation (among many) were considered to be the most feasible. Many of the undesirable heavy metals form soluble amines, whereas iron, calcium and aluminum do not. The cake could therefore be slurried with a small amount of relatively strong ammonium hydroxide, filtered, and the filtrate should contain most of the zinc, copper, and chromium. However, a certain amount of phosphate might also be solubilized, although this might be only a minor fraction of the total. The filter cake, now free of most of the undesirable heavy metals, could then have the phosphate and iron separated by treatment with sodium hydroxide which would solubilize the phosphate but not the iron.

Alternately, the filter cake from the selective precipitation could be treated with sodium hydroxide directly. It was this alternative which was investigated in this work.

8.1 Separation of Metals and Phosphates in Alkaline Solution

Portions of filter cake were slurried in sodium hydroxide solutions of various strengths, in amounts such that the resulting solutions could have a maximum soluble phosphate concentration of about 0.03 molar. The pH was measured after stirring for 20-30 minutes and the solution was then sampled and analyzed for phosphorus, aluminum, zinc and calcium if significant. Results are shown in Figure 11. It is interesting to note that at the concentration levels used all the aluminum and most of the phosphate can be solubilized at pH 13.5, with only a small fraction of the zinc also going into solution. No iron was found in the solution.

In order to generalize these results, data were sought on the two reactions in which aluminum and zinc form so-called "aluminate" (AlO_2^-) or "zincate" ($ZnO_2^=$) ions in sodium hydroxide solutions, (probably these ions are more correctly written as $Al(OH)_4^-$ and $Zn(OH)_4^=$, respectively). According to Cotton and Wilkinson (4), the formation of aluminate ions can be written:

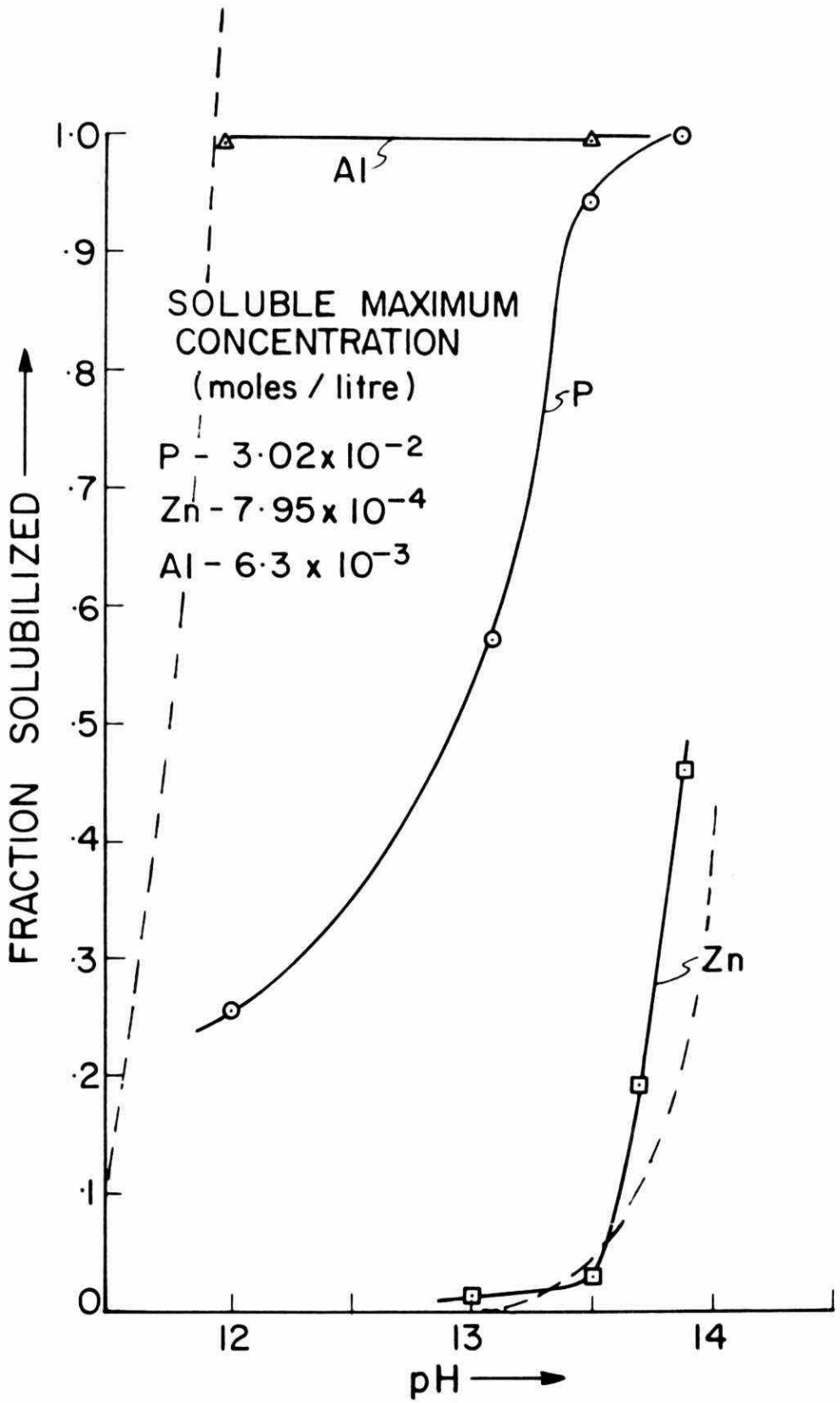

FIGURE 11. SEPARATION OF IRON AND PHOSPHATE BY SODIUM HYDROXIDE SOLUTIONS

$$Al(OH)_3(s) \rightarrow AlO_2^- + H^+ + H_2O \qquad K = 4 \times 10^{-13}$$

The calculated solubility of aluminum as a function of pH is plotted also in Figure 11, as shown by the dashed line. A similar equilibrium constant has been reported by Pascal (9) for the corresponding reaction

$$Zn\ O + 2OH^- + H_2O = Zn(OH_4)^= \qquad K = 10^{-2}$$

Another value as reported by Sillen and Martell (13) is for the reaction

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^= \qquad K = 10^{-1.74}$$

However, from the experimental results shown on Figure 11, K would appear to have a value of about $10^{-3.4}$ for the above reaction. Using this value, the solubility of zinc in sodium hydroxide was also calculated and is shown in Figure 11. Clearly, a good separation between aluminum and zinc is possible, with good recovery of orthophosphate in the solution. Since the aluminum is non-toxic to plant or animal life, its presence in the phosphate containing solution might be tolerable.

In more concentrated phosphate solutions, considerable amounts of zinc as well as the aluminum might go into solution because higher pH values would be needed for higher phosphate solubilization. In this case, further treatment would depend on the commercial form desired for the phosphate, for example, as trisodium orthophosphate, orthophosphoric acid, etc.

It is probable that the phosphate in the cake might also be solubilized and separated from the iron by treatment with strong ammoniacal solutions. This possibility was not investigated.

When precipitation of the extract whose composition is given in Table 5 was carried out to a pH of 7.0 using lime rather than sodium hydroxide, and the filter cake treated with sodium hydroxide, the results obtained were essentially the same as those shown in Figure 11. As expected, very little lime went into solution.

9. COST CONSIDERATIONS

In any process for removing metals or phosphates from sludge, the principal metal will usually be iron (or perhaps aluminum) by a large margin. Similarly, phosphate appears to be the objectionable anion present in largest quantity. Both iron salts and phosphates are cheap bulk commodities, and since bulk chemical reagents (acid and lime) in at least equivalent amounts must be used to separate them from the sludge, it might be expected that reagent costs would be nearly equal to the value of the recovered material. Therefore, as is typical of wastewater treatment processes, the removal of metals and phosphates from sludges must be justified on a cost-benefit basis, and not on a profit basis.

If it is assumed that a need may arise to remove phosphate and some of the heavy metals from sludge, then the costs of rendering the sludge innocuous can be estimated. While these estimates are necessarily rather crude, the cost of preparing the filter cake containing most of the metals and phosphate, and having a composition similar to that given in Table 8 is about 1.0¢/lb of dry sludge for capital costs and about 1.78¢ for operating costs, including reagents, steam, labour, overhead etc. These figures were obtained by an order of magnitude estimate, using as a base a plant of 100 mgd capacity which produces by anaerobic digestion 1200 lb of dry sludge solids in the digester underflow per million gallons of influent. Hence, the cost of rendering a sludge largely free of metals and phosphates would be of the order of $30 - $35 per million gallons of influent. This would yield a sludge low in metals and phosphate, filtrates containing soluble organics only, and a solid product which would be 70-80% ferric phosphate (where iron is used for phosphate removal or as a coagulant). Costs for removal of metals from sludges produced by plants using alum for phosphate removal or coagulation would be very similar.

The crude ferric phosphate cake produced can be treated in several ways. Two possibilities were investigated in this work. Separation by dissolution in alkali yields a ferric hydroxide which then must be dissolved in sulphuric acid to make a soluble ferric sulphate for recycling. The soluble phosphate would be recovered possibly as trisodium phosphate. Rough estimates for this process suggest total costs of about 3.0 cents per lb.

of dry sludge. The value of the products obtained, on the basis of a credit of 12-1/2 cents per pound of iron for soluble iron and 82 cents per pound of phosphorus for a sodium phosphate would be 3.79 cents/lb of dry sludge solids, yielding a net credit of about 0.8 cents/lb of dry sludge or about $10 per million gallons of influent.

A second alternative for treating the crude ferric phosphate would be by use of conventional solvent extraction techniques to produce a ferric chloride product and a technical grade 75% phosphoric acid. Using the same value for soluble iron as before, and 50 cents per pound of phosphorus for a technical phosphoric acid, the value of the products would be 2.65 cents/lb of dry sludge solids. For the solvent extraction process shown in Figure 10, reported processing costs from the literature combined with acid and solvent make-up costs suggest a total operating plus capital cost for a relatively small installation of about 1.7¢ per lb of dry sludge solids. This process would result in a net credit of about 0.95 cents per pound of sludge or about $11 per million gallons.

In all of these costs, the fraction represented by reagents is from 60% - 80% of the total, and there would seem to be relatively little scope for reduction of this component. In summary, the net cost of removing metals and phosphates from an anaerobic unconditioned sludge, and recovering the iron and phosphate for recycling would be in the neighborhood of $20-$25 per million gallons of influent. Since the major expenditure is for reagents, this net cost would increase or decrease only a small amount for smaller or larger plants than 100 mgd, or for increased or decreased metal and phosphate contents.

Further studies would be required to determine if the cost of removing metals and phosphates from sludge is commensurate with the benefits obtained. If for some reason it is necessary to remove these components from a sludge, then it is profitable to also recycle at least the iron and the phosphate. With the method developed in this study, it is not a profitable process to recover and recycle iron and phosphate for its own sake.

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